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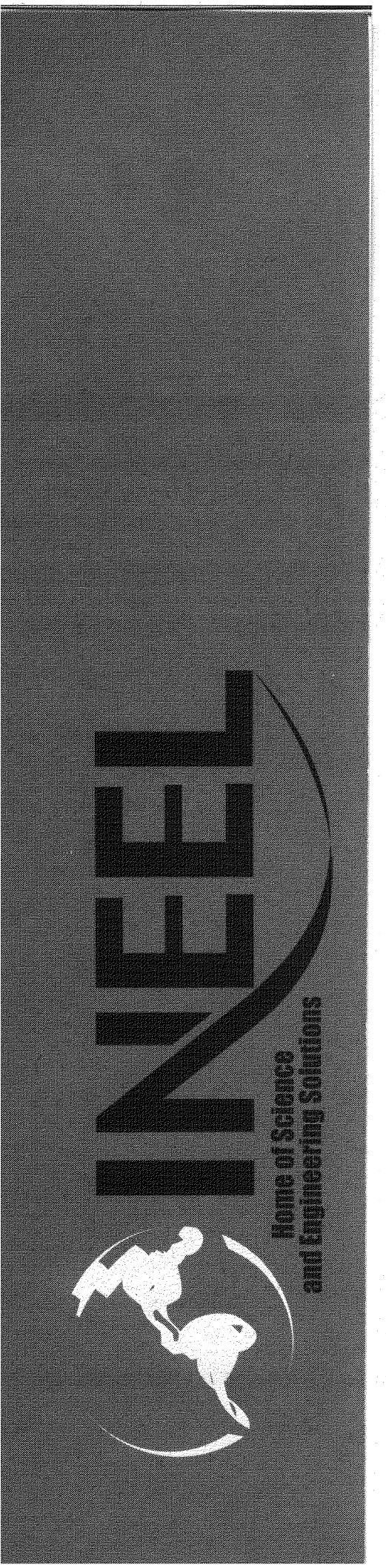

Annual Performance Report for In Situ Bioremediation Operations August 2001 to October 2002, Test Area North Operable Unit 1-07B

September 2003

Idaho National Engineering and Environmental Laboratory
Bechtel BWXT Idaho, LLC

INEEL/EXT-03-00371
Revision 0

Project No. 23339

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September 2003

Idaho National Engineering and Environmental Laboratory
Idaho Completion Project
Idaho Falls, Idaho 83415

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Assistant Secretary for Environmental Management
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ABSTRACT

This reports presents the activities performed and data collected during the operation of the enhanced in situ bioremediation remedy component at the Operable Unit 1-07B source area for the reporting period August 2001 to October 2002. In general, activities consisted of continued sodium lactate injection and groundwater monitoring. Several sodium lactate injection strategies were tested to achieve the desired electron donor distribution and dechlorination activity within the source area. Additional activities, including groundwater modeling, a tracer test, and laboratory evaluation of alternate electron donors, were performed.

The results indicate that, in general, the in situ bioremediation remedy is operating effectively, stimulating complete dechlorination throughout most of the secondary source. Trichloroethene and cis-DCE concentrations remained low, and ethene was the dominant compound at several source area wells. However, the results from downgradient wells indicated that the injection strategies used during the reporting period, including very large volume injections, still did not distribute electron donor or stimulate dechlorination activity throughout the entire secondary source in the downgradient direction. Further, spikes in cis-DCE in some source area wells following large volume injections indicated that the injection of large volumes of potable water was negatively impacting the anaerobic microbial community near TSF-05. This observation was accompanied, however, by indicating that conditions were becoming more reducing downgradient. While an apparent decline in anaerobic reductive dechlorination efficiency was observed, the results of the tracer test and groundwater modeling suggest that the operation of in situ bioremediation over the past 4 years has had a positive impact on the secondary source material, indicating that is situ bioremediation is actively removing the secondary source.

Based on these results, it is concluded that a second injection well located downgradient of TSF-05 remains necessary, in addition to TSF-05, in order to achieve the desired distribution of electron donor. Also, it is recommended that several alternate electron donors be further evaluated for their potential effectiveness compared to lactate.

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ACRONYMS

AED	alternate electron donor
ARD	anaerobic reductive dechlorination
B.E.T.™	Bioavailability Enhancement Technology™
COD	chemical oxygen demand
DCE	dichloroethene
DHE	*dehalococcoides ethenogenes*
DNAPL	dense nonaqueous phase liquid
DQO	data quality objective
EPA	Environmental Protection Agency
IFT	interfacial tension
INEEL	Idaho National Engineering and Environmental Laboratory
IRC	INEEL Research Center
ISB	in situ bioremediation
MCL	maximum contaminant level
MDA	minimum detectable activity
MNA	monitored natural attenuation
MS/MSD	matrix spike and matrix spike duplicate
NPTF	New Pump and Treat Facility
ORP	oxygen reduction potential
ou	operable unit
PCE	tetrachloroethene
PCR	polymerase chain reaction
PDO	predesign operation
PDP	predesign phase
PE	performance evaluation

QA	quality assurance
QA/QC	quality assurance/quality control
RAO	remedial action objective
RML	Radiation Measurements Laboratory
RPD	relative percent difference
SAP	sampling and analysis plan
SVOC	semi volatile organic compound
T-RFLP	terminal restriction fragment length polymorphism
TAL	Target Analyte List
TAN	Test Area North
TCE	trichloroethene
TSF	Technical Support Facility
VC	vinyl chloride
VFA	volatile fatty acid
VOA	volatile organic analyte
VOC	volatile organic compound

Annual Performance Report for In Situ Bioremediation Operations August 2001 to October 2002, Test Area North Operable Unit 1-07B

1. INTRODUCTION

A nearly 2-mile long plume of trichloroethene (TCE) in groundwater is located at the Test Area North (TAN) facility of the Idaho National Engineering and Environmental Laboratory (INEEL). Due to the size and varying TCE concentrations of the plume, a multi-component remedy was designed to achieve effective cleanup. Enhanced in situ bioremediation (ISB) was selected for remediation of the source area portion of the plume, and bioremediation activities have been ongoing since 1999. This annual report provides a summary of ISB activities conducted at the Operable Unit (OU) 1-07B hot spot for the reporting period August 2001 to October 2002.

1.1 Report Purpose and Organization

The purpose of this report is to document the evaluation of the progress of ISB activities implemented in the OU 1-07B hot spot as measured against the objectives presented in the governing documents. The period of evaluation covered by this report is from August 2001 to October 2002.

This report contains nine sections and five appendices. Section 1 presents an overview of the ISB remedy component and specifies the governing documents for the performance period. Section 2 presents the objectives for the data collection and evaluation activities. Section 3 describes the activities performed; Section 4 presents the results of these activities. Section 5 discusses the results in the context of the objectives, while Sections 6 through 8 present the conclusions and recommendations for additional activities and provide suggested reporting guidance for future reports written under the *In Situ Bioremediation Remedial Action Work Plan for Test Area North Final Groundwater Remediation, Operable Unit 1-07B* (DOE-ID 2003a). References are included in Section 9, and the six appendices contain supporting information, as indicated throughout the main text. A CD-ROM is attached, which contains all ISB data collected during the approximately 4 years of ISB operations.

1.2 Overview of the In Situ Bioremediation Remedy Implementation

As stated above, OU 1-07B consists of a nearly two-mile-long plume of TCE in groundwater emanating from the Technical Support Facility (TSF)-05 injection well. Due to the large scale and the varying contaminant concentrations within the plume, the plume has been divided into three zones (Figure 1-1): the hot spot, medial zone, and distal zone. A multi-component remedy was designed to address each of these three zones, as described in the *Record of Decision Amendment for the Technical Support Facility Injection Well (TSF-05) and Surrounding Groundwater Contamination (TSF-23) and Miscellaneous No Action Sites Final Remedial Action* (DOE-ID 2001):

- Hot spot—ISB (anaerobic reductive dechlorination [ARD])
- Medial Zone—Groundwater pump and treat
- Distal Zone—Monitored natural attenuation (MNA).

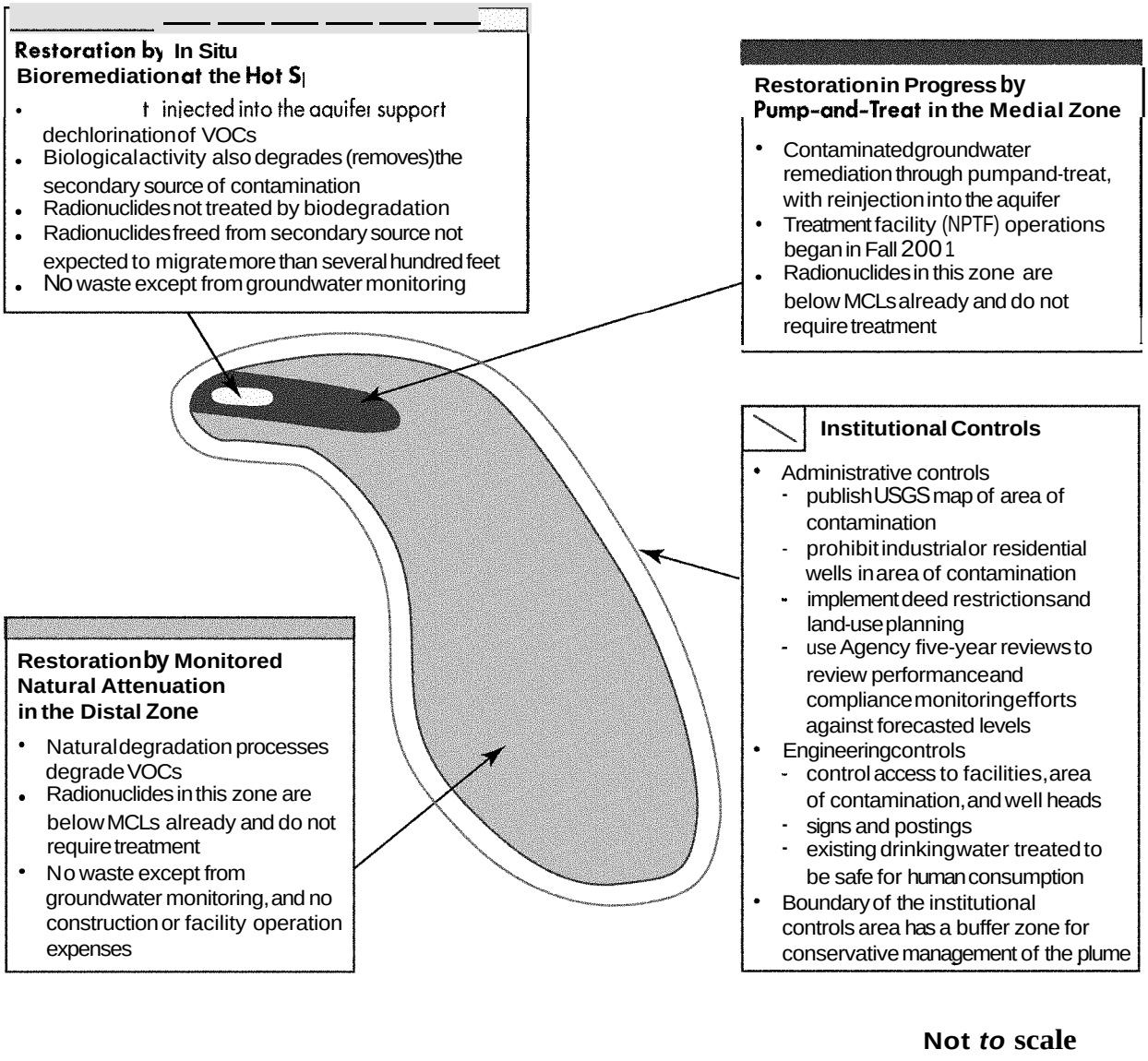
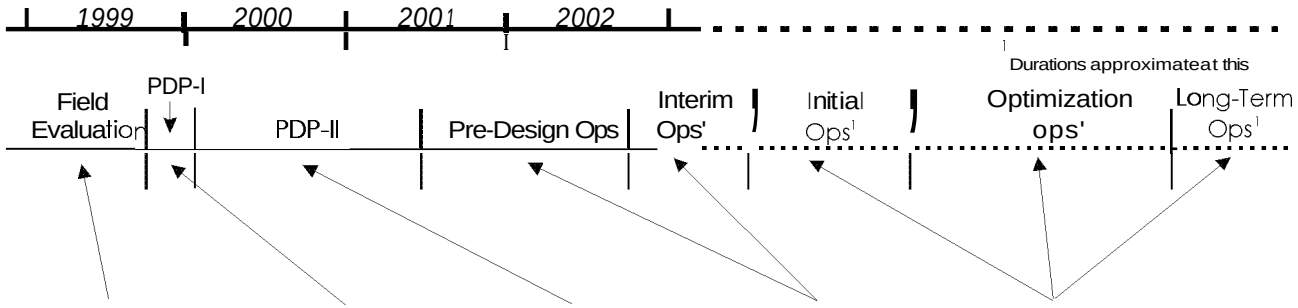


Figure 1-1. Conceptual illustration of the three zones of the TCE plume.

This section provides a review of the ISB implementation process. It includes a summary of ISB activities conducted up through the last annual report (July 2001), the activities covered by this report (August 2001 through October 2002), and hture activities (November 2002 and beyond). Figure 1-2 presents an overview of the phases used for the implementation of ISB in the hot spot. The specific objectives for the period of performance covered by this report are presented in detail in Section 2.



Overall Objectiv	Determine TCE could be enhanced the addition of electron	Monitor reactions propionate fermentation conditions in absence of lactate	Recreate the conditions for efficient observed PDP-I	Continue to operate ISB while optimization achieve cost	Continue operation, while reducing eventually eliminating down- and cross-gradient flux VOCs from the
Operation	Small, frequent (weekly/biweekly) lactate injections; groundwate monitoring	No lactate injections; groundwate monitoring	Relatively volume, (bimonthly) injections; groundwate monitoring; studies.	Relatively volume, (bimonthly) injections; groundwate monitoring; studies.	Implement strategy based on and Interim Ops groundwate monitoring
Results	Complete ARD ethene ISB selected as hotspot	ARD increased propionate utilization in the absence lactate fermentation	In general, conditions for maintained; however, of lactate downgradient problematic	In general, conditions for maintained; however, of lactate downgradient problematic	TB
Controlling Documen	Field Work	Field Work	Field Work	PDO WP Remedial Action	Remedial Action Plan
Reports	FDR/FE	01 Annual	01 Annual	01 Annual current report, and future	Annual Compliance

Figure 1-2. Overview of the phases used for in situ bioremediation implementation in the hot spot.

1.2.1 Summary of In Situ Bioremediation Activities through the Previous Annual Report (July 2001)

In situ bioremediation activities began in November 1998 with the field evaluation. The overall objective of the field evaluation was to determine whether ARD of TCE could be enhanced through the addition of an electron donor (lactate). Nine months of sodium lactate injection in well TSF-05 and groundwater monitoring throughout the treatment cell produced sufficient data to conclude that ARD was significantly enhanced, and ISB was officially selected as the hot spot remedy. A complete discussion of the results of the field evaluation is presented in the *Field Demonstration Report, Test Area North Final Groundwater Remediation, Operable Unit 1-07B* (DOE-ID 2000). Following this initial testing phase, activities shifted toward optimization of the ISB remedy. This began in October 1999 with Predesign Phase (PDP) -I activities, which consisted of no sodium lactate injections and continued groundwater monitoring throughout the hot spot. The objective of PDP-I was to see how the system would respond to the absence of regular sodium lactate injections, while only the electron donor (mainly propionate) already present from the field evaluation injections was utilized. The results indicated an increase in the efficiency of ARD reactions during this time of propionate fermentation. PDP-I was ended when most of the electron donor present from the field evaluation was depleted, and additional lactate injections were needed.

Based on the PDP-I results, an injection strategy that maximized the time of propionate fermentation and minimized the time for lactate fermentation was designed for PDP-II. It was the objective of PDP-II to recreate the favorable conditions for efficient ARD observed during PDP-I and to determine the best injection strategy for later phases. PDP-II, beginning in February 2000, consisted of the injection of relatively large volumes of electron donor relatively infrequently (every 8 weeks) compared to the smaller volume; more frequent injections (weekly/biweekly) were used during the field evaluation. The results of PDP-II indicated that in general, good conditions for ARD were created with this injection strategy; however, the distribution of electron donor to the downgradient area of the source remained problematic. A complete discussion of the results of PDP-I and PDP-II is presented in the *OU 1-07B ISB Annual Performance Report for October 1999 to July 2001* (INEEL 2002a). Shortly after the onset of PDP-II, laboratory studies were initiated to evaluate alternative, potentially less expensive electron donors for their ability to support efficient ARD and to enhance degradation of the secondary source, with the objective of designing the most cost-effective remedy.

The implementation of the next phase of activities, predesign operations (PDO), was initiated in May 2001 with the completion of the *In Situ Bioremediation Predesign Operations Work Plan Test Area North, Operable Unit 1-07B* (INEEL 2002b). In general, the objectives of PDO were to continue the optimization of the ISB remedy through continued operations (sodium lactate injection and groundwater monitoring) and experimentation with various injection strategies. The results of PDO through July 2001 were presented in the Fiscal Year 2001 Annual Performance Report (INEEL 2002a).

1.2.2 Activities Presented in this Report (August 2001 to October 2002)

The ISB activities presented in this report were conducted under the PDO Work Plan (INEEL 2002b). As stated above, the overall goal of PDO was to optimize the ISB remedy. The specific objectives of the PDO phase are presented in detail in Section 2 of this report. Activities for this reporting period consisted of the continued injection of electron donor to achieve the desired distribution and to create the conditions for efficient ARD throughout the source zone. The evaluation of alternate electron donors (AEDs) in laboratory studies initiated with the onset of PDO was also completed during the current reporting period.

1.2.3 Future Activities (November 2002 and Beyond)

As shown in Figure 1-2, the PDO phase ended in October 2002 and is followed by a series of phases governed by the *In Situ Bioremediation Remedial Action Work Plan for Test Area North Final Groundwater Remediation, Operable Unit 1-07B,* (DOE-ID 2003a). A summary of these phases and their objectives and operations are presented below, while a complete description is presented in the Remedial Action Work Plan.

- Interim Operations Phase—This phase will essentially be a continuation of the PDO objectives and will cover activities that support a better understanding of AEDs (potentially including a field pilot test), development of injection strategies that support the Initial Operations Phase, ISB model refinement, and continued ISB sodium lactate addition.

- Initial Operations Phase—This phase will focus on reducing the flux of volatile organic compounds (VOCs) from the hot spot in the downgradient direction. During this phase, data will also be gathered and analyzed relating to achievement of long-term performance objectives.

- Optimization Operations Phase—This phase will focus on reducing the flux of VOCs from the hot spot in the crossgradient direction, while maintaining VOC flux reduction in the downgradient direction.

- Long-Term Operations Phase—During this phase, data will continue to be gathered and analyzed relating to achievement of long-term performance objectives. This phase will focus on achievement of hot spot source degradation, while maintaining the reduction of VOC flux from the hot spot in the crossgradient and downgradient directions. The Remedial Action Work Plan presents the criteria for completion of each phase, as well as performance monitoring and compliance monitoring requirements for each phase. Progress of ISB activities against these requirements will be the focus of hture reports.

1.3 Governing Documents

As described above and shown in Figure 1-2, the governing document for the performance period covered by this report is the PDO Work Plan (INEEL 2002b). This is supported by the *Sampling and Analysis Plan for Enhanced In Situ Bioremediation Predesign Operations Test Area North, Operable Unit 1-07B* (INEEL 2001), which provides specific information related to the sampling and analysis activities. The governing documents for hture phases beginning with Interim Operations, which began in November 2002 are the Remedial Action Work Plan (DOE-ID 2003a) and supporting documents, specifically the *In Situ Bioremediation Remedial Action Groundwater Monitoring Plan for Test Area North, Operable Unit 1-07B* (INEEL 2002b) and the *ISB Operations and Maintenance Plan for Test Area North, Operable Unit 1-07B* (DOE-ID 2002a).

2. OBJECTIVES

The ultimate goal of OU 1-07B remedial activities is to achieve the remedial action objectives (RAOs). The RAOs specified in the Record of Decision (ROD) Amendment (DOE-ID 2001) are as follows:

- Restore the contaminated aquifer groundwater by 2095 (100 years from the signature of the Record of Decision for the Technical Support Facility Injection Well (TSF-05) and Surrounding Groundwater Contamination (TSF-23) and Miscellaneous No Action Sites Final Remedial Action [DOE-ID 19951) by reducing all contaminants of concern (COCs) to below maximum contaminant levels (MCLs) and a 1×10^{-4} total cumulative carcinogenic risk-based level for hture residential groundwater use and, for non-carcinogens, until the cumulative hazard index is less than 1.

- For aboveground treatment processes in which treated effluent will be reinjected into the aquifer, reduce the concentrations of VOCs to below MCLs and a 1×10^{-5} total risk-based level.

- Implement institutional controls to protect current and hture users from health risks associated with (1) ingestion or inhalation of, or dermal contact with, contaminants in concentrations greater than the MCLs, (2) contaminants with greater than a 1×10^{-4} cumulative carcinogenic risk-based concentration, or (3) a cumulative hazard index of greater than 1, whichever is more restrictive. The institutional controls shall be maintained until concentrations of all COCs are below MCLs and until the cumulative carcinogenic risk-based level is less than 1×10^{-4} and, for noncarcinogens, until the cumulative hazard index is less than 1. Institutional controls shall include access restrictions and warning signs.

As described in Section 1.2, the implementation of ISB in the hot spot to achieve these RAOs has been divided into individual phases with specific objectives for each phase. The phase of activities for the period of performance discussed in this report is the PDO phase. The overall goal of the PDO phase was to collect data to support the most efficient and cost-effective ISB system design for later phases. The specific objectives, as presented in the PDO Work Plan (INEEL 2002b), and the activities conducted to achieve these objectives are presented in Table 2-1. This report discusses the results of these activities in the context of the objectives.

Future phases are designed with the objectives of reducing flux in the downgradient and crossgradient directions and developing the most cost-effective strategy for long-term operations of the ISB remedy component (DOE-ID 2002a). The operations in these subsequent phases are conducted under the Remedial Action Work Plan and performance during these phases will be evaluated in annual performance and compliance monitoring reports. Guidance for the preparation of these reports is presented in Section **8** of this report.

Table 2-1. Predesian operation obiectives and activities from the Predesian Operation Work Plan.

Objective	Activities
A. Continue to operate the ISB system to contain and degrade the ISB hot spot	• Continued ISB system operation (sodium lactate injection and groundwater monitoring)
B. Maximize cost-effectiveness of TCE dechlorination	• Optimize electron donor injection volume, concentration, and frequency • Verify effectiveness of injection strategy using groundwater monitoring data • Use modeling to optimize the final ISB treatment system design and operating strategy
C Optimize the sampling frequency and analytes	• Evaluate the cost-effectiveness and utility of each analytical parameter against the data quality objectives (DQOs) • Determine the most cost-effective sampling frequency to meet the DQOs
D Determine whether sodium lactate injection results in mobilization of metals, strontium, and/or semivolatile organic compounds (SVOCs) from the secondary source (defined as an objective for all predesign phases in the Enhanced In Situ Bioremediation Field Evaluation Work Plan, Test Area North, Operable Unit 1-07B [DOE-ID 19981, Appendix E)	• Continued implementation of ISB system operations • Monitor concentrations of gamma emitters, alpha emitters, metals, strontium, and tritium. (SVOC monitoring was completed prior to this reporting period)
E. Determine how to better distribute electron donor within the upper part of the aquifer (defined in the Field Evaluation Work Plan [DOE-ID 1998, Appendix E] for PDP-III)	• Use modeling to evaluate injection strategies • Characterize the changes to the flow and transport system in the source area using a tracer test • If necessary, implement the activities of PDP-III, which would involve the injection of electron donor in Well TAN-37, and/or the use of alternative electron donors
F. Determine the effectiveness of alternative electron donors relative to lactate for sustaining anaerobic reductive dechlorination reactions within the aquifer (defined in the Field Evaluation Work Plan [DOE-ID 1998, Appendix E] for PDP-III).	• Conduct laboratory studies evaluating various alternative electron donors.

3. ACTIVITIES PERFORMED

This section provides a description of the activities conducted during operation of the ISB remedy component for the reporting period. These activities included electron donor injection operations (Section 3.1), groundwater sampling (Section 3.2), on-Site and off-Site sample analysis (Section 3.2), waste management (Section 3.3), groundwater modeling (Section 3.4), the 2002 Tracer Test (Section 3.5), alternate electron donor laboratory studies (Section 3.6), and ISB operational support activities (Section 3.7). The following sections describe the work performed during the execution of these activities for the reporting period.

3.1 Electron Donor Injection Operations

This section describes operations pertaining to electron donor injection, including the dates of injections and sodium lactate sampling and analysis. Sodium lactate injection operations were performed in accordance with TPR-163, "Nutrient Injection System Operating Procedure," which details the equipment and procedures used to perform injections. Sodium lactate was brought on site as a 60% solution (by weight) in 55-gal drums. Injections were performed by pumping directly from the drums into a flowing potable water line, which allowed for in-line mixing, and injecting into TSF-05. Sodium lactate injection dates, volumes, and concentrations during the reporting period are shown in Table 3-1. The column "injection type" refers to the approximate volume of sodium lactate plus potable water that was injected, as well as the intended nominal sodium lactate concentration. The actual concentrations calculated based on volumes injected are presented in the column "resultant sodium lactate concentration." A 1X injection was defined as approximately 12,000 gal total volume, 2X as 24,000 gal, and 4X as 48,000 gal. JRW Technologies was the only sodium lactate vendor used during this reporting period. All of the stock products were 60% by weight (w/w) solutions of sodium lactate.

Table 3-1. Sodium lactate injections during the reporting period.

Injection Date	Volume 60% (w/w) Sodium Lactate Injected (gal)	Injection Type	Total volume Sodium Lactate Solution Injected (gal)	Resultant Sodium Lactate Concentration	Combined Injection Flow Rate (gpm)	Potable Water Flush Volume (gal)
September 5, 2001	1,320	1X 6%	12,000	6.6	40	2,280
October 30, 2001	1.320	2 x	23,096	3.4	38	2,280
January 2, 2002	1,320	2 x	20,502	3.9	38.48	2,280
March 25-28, 2002	5,280	4 x	52,800	6.0	40	9,120
July 1, 2002	1,320	1X	13,200	6.0	40	2,160
July 30-31, 2002	2,640	4 x	46,740	3.4	38	4,320
October 1-3, 2002	2.640	4 x	46,536	3.4	40	6,840

Sodium lactate injection concentrations were modified between 3.0 and 6.0% (nominal concentrations) during the reporting period. These modifications were made in an effort to experiment with different electron donor concentrations to improve ARD efficiency while avoiding density differences sufficient to cause the injected sodium lactate solution to sink to the base of the aquifer before being utilized.

During the treatment and disposal of sample water that was being stored in Groundwater Treatment Facility (GWTF) *tank* T-1 (described in Section 3.7.2), approximately 50 gal of 60% sodium lactate were added to 5,000 gal of flush water to produce a 0.6% sodium lactate solution. This solution was injected into well TAN-31.

Environmental Protection Agency (EPA) Target Analyte List (TAL) metals in sodium lactate were measured in three batches of sodium lactate received from JRW to ensure that concentrations did not exceed allowable levels that were defined during the field evaluation as 10 x MCLs (DOE 1998, Attachment 1). This acceptance level was based on the requirement of not injecting concentrations of regulated substances in sodium lactate that would result in concentrations above MCLs in TAN production wells. Two batches for which metals were analyzed were received during this reporting period, and one batch was analyzed for metals prior to August 2001. Results are presented in Section 4.2 of this report.

3.2 Groundwater Sampling and Analysis

This section summarizes groundwater sampling and analysis activities for the reporting period, including an overview of the monitoring program, sampling schedule and deviations, on-Site and off-Site analyses, in situ geochemical monitoring, and water level monitoring. Additional details for the information presented in this section are provided in Appendix A; Sampling and Analysis Plan (SAP) tables used during this reporting period are provided in Appendix B (see attached CD-ROM); and additional in situ geochemical monitoring equipment operation details are provided in Appendix C.

3.2.1 Overview of Monitoring Program

As stated in Section 1.3, the documents governing all work performed during this reporting period are the PDO Work Plan (INEEL 2002b) and the PDO SAP (INEEL 2001). These two documents describe the implementation of ISB, which includes extensive groundwater monitoring throughout the treatment cell. All monitoring wells were purged prior to sample collection following low-flow sampling principles according to TPR-165, "Low Flow Groundwater Sampling Procedure." Sampling equipment included the use of variable speed submersible pumps operated at approximately 3.8 L/min (1 gpm); sample boards equipped with tubing, appropriate fittings for well riser pipes, detachable sample ports, and flow through cells to accommodate a multiparameter water quality instrument, and containers for purge water. Fourteen monitoring locations were sampled monthly (Table 3-2), and the analytes for each monthly sampling event are stated in Section 3.2.2. Analyses were performed using a combination of on-Site and off-Site laboratories and in situ monitoring. On-Site analyses conducted in the ISB Field Laboratory were performed according to TPR-166, "ISB Field Analyses Procedures."

Table 3-2 details the 14 monitoring locations, the depth of each sampling point, and the horizontal distance of each point from the TSF-05 injection well. It should be noted that wells TSF-05 and TAN-37 utilized sampling points located at multiple depths within the borehole. In these cases, a letter (A, B, or C) was used to distinguish between the specific sampling depths. Of these 14 monitoring locations, seven wells were identified as the ISB source mobility monitoring wells, including TSF-05A, TSF-05B, TAN-25, TAN-26, TAN-31, TAN-28, and TAN-29. Since these wells are located along the axis of the plume, these data were used to identify if radionuclides and/or metals have been mobilized from the TSF-05 source area.

Table 3-2. Wells sampled during in situ bioremediation sampling events.

Well	Depth Sampled (ft)	Distance from TSF-05 (ft)
TSF-05A[a]	235	0
TSF-05B[a]	275	0
TAN-25	218	25
TAN-26	389	50
TAN-27	235	320
TAN-28	242	262
TAN-29	253	513
TAN-30A	313	271
TAN-31	258	50
TAN-37A[a]	235	148
TAN-37B[a]	272	148
TAN-37C[a]	379	148
TAN-10A	233	179
TAN-D2	241	115

a. Wells TSF-05 and TAN-37 are sampled at more than one depth. The letter following the well number is used to represent the sample depth.

3.2.2 Sampling Schedule and Deviations

The sampling dates for routine ISB sampling and analysis for the period from August 2001 to October 2002 are shown in Table 3-3. Table 3-4 shows analytes and analysis locations. As stated above, a monthly monitoring frequency was used throughout the reporting period. In general, all 14 ISB wells listed in Table 3-2 were monitored for a standard suite of analytes selected to provide sufficient data to evaluate the progress of the bioremediation system. Also, several supplemental and quality assurance (QA) parameters were included on a less frequent basis or from select monitoring locations to address specific needs. SAP tables were used to record all pertinent information associated with each groundwater sample collected and are provided in Appendix B (see attached CD-ROM).

Deviations from the sampling schedule, shown in Table 3-3, occasionally occurred during the reporting period. Deviations included samples not collected as a result of equipment malfunctions, container breakage, omission of blanks, overestimation of the number of blanks needed, and additional samples collected to fulfill nonroutine project needs. Deviations are listed chronologically in Appendix A.

During all phases of ISB activity, samples from TAN-25, TAN-26, TSF-05A, and TSF-05B have routinely been screened for gamma activity before shipping samples off-Site. However, riser pipe in TAN-31 was found to be radiologically contaminated following well maintenance activities conducted in late August 2001. Therefore, starting with the September 10–11, 2001, sampling round, TAN-31 was also included for gamma screening before shipping samples off-Site.

Table 3-3. In situ bioremediation sampling and analysis dates for the reporting period

Date	Analyte Set[a]	Sampling Location[b]
August 6–8,2001	M, Sp	All ISB wells (TAN-37C not included), Gamma Screen not included for TAN-31
	Mt, ^{90}Sr, GS	ISB source mobility monitoring wells
	MB_1	Well TAN-25
	MB_2	Wells TAN-25, 28, 29, 30A, 31, 10A, 37A, and 37B
September 10–11,2001	M	All ISB wells (TAN-37C not included)
	MB_1	Well TAN-25
	MB_2	Wells TAN-25, 28, 29, 30A, 31, 10A, 37A, and 37B
October 8 and 0,2001	M	All ISB wells (TAN-37B not included)
	MB_1	Well TAN-25
	MB_2	Wells TAN-25, 28, 29, 30A, 31, 10A, 37A and 37C
November 5–7,2001	M, Sp, N	All ISB wells (TAN-37B collected on November 19, 2001, as an interim sampling event)
	Mt, ^{90}Sr, GS, GA	ISB source mobility monitoring wells
	MB_1	Well TAN-25
	MB_2	Wells TAN-25, 28, 29, 30A, 31, 10A, 37A and 37C.
November 19,2001	M (included samples for all analytes except tritium)	Well TAN-37B
December 3–6 and 0,2001	M	All ISB wells (TAN-37B collected on December 10.2001)
	MB_1	Well TAN-25
	MB_2	Wells TAN-25, 28, 29, 30A, 31, 10A, 37A and 37C
January 7–9,2002	M	All ISB wells
	MB_1	Well TAN-25
	MB_2	Wells TAN-25, 28, 29, 30A, 31, 10A, 37A, 37B, and 37C

Table 3-3. (continued).

Date	Analyte Set[a]	Sampling Location[b]
February 4–6,2002	M, Sp (splits not included for TAN-37B)	All ISB wells
	Mt (also included TAN-37B), GS, ^{90}Sr	ISB source mobility monitoring wells
	MB_1	Well TAN-25
	MB_2	Wells TAN-25, 28, 29, 30A, 31, 10A, 37A, and 37C
March 4–5,2002	M	All ISB wells (TAN-37B not included)
	MB_1	Well TAN-25
April 1–3,2002	M	All ISB wells
	MB_1	Well TAN-25
April 17, 2002	M (included samples for all analytes except tritium)	Only Wells TAN-37A, B, and C (taken after a 4X sodium lactate injection as an interim sampling event midway between 2 ISB sampling events)
April 29–May 1,2002	M, Sp, N	All ISB wells
	Mt (filtered, also included TAN-37B), GS, ^{90}Sr	ISB source mobility monitoring wells
	MB_1	Well TAN-25
May 8,2002	MB_1	Well TAN-25 (collected as an interim sampling event)
June 3–4.2002	M	All ISB wells
	B, I	Wells TAN-25 and 31
	MB_1	Well TAN-25
	FSA	Wells TAN-10A
July 8–10,2002	M	All ISB wells
	B, I	Wells TAN-25 and 31
	FSA	Well TAN-10A
	MB_1	Well TAN-25
August 5–6,2002	M, Sp	All ISB wells
	FSA	Well TAN-D2
	Mt (filtered, also included TAN-37B), GS, ^{90}Sr	ISB source mobility monitoring wells
	MB_1	Well TAN-25
September 9, 2002	M	All ISB wells
	FSA	Well TAN-10A
	MB_1	Well TAN-37C
	I	Well TAN-37A and 37B

Table 3-3. (continued).

Date	Analyte Set[a]	Sampling Location[b]
October 7–8, 2002	M	All ISB wells
	FSA	Well TAN-26
	I	Well TAN-37A and 37B

a. The analyte set key is provided in Table 3-4.

b. All ISB wells include: TSF-OSA, TSF-OSB, TAN-25, TAN-26, TAN-27, TAN-28, TAN-29, TAN-30A, TAN-31, TAN-37A, TAN-37B, TAN-37C, TAN-10A, and TAN-D2.

The ISB source mobility monitoring wells include: TSF-OSA. TSF-OSB. TAN-25. TAN-26. TAN-31. TAN-28. and TAN-29.

'able 3-4. Key or analyte sets shown in Table 3-3.

Analyte set code	Analytes	Analysis location
B	Bromide	In Situ Bioremediation (ISB) Field Laboratory
I	Iodide	
FSA	Field Standard Additions	
M	**ISB monthly monitoring analyte list:** Volatile organic compounds (VOCs): includes trichloroethene (TCE), tetrachloroethene (PCE), cis-1,2-dichloroethene (cis-DCE), trans-1,2-dichloroethene (trans-DCE), and vinyl chloride (VC)	INEEL Research Center (IRC)
	Ethene/ethane/methane	
	Propionate/Butyrate/Acetate/Lactate	
	Tritium	Off-Site laboratorv
	Alkalinitv	ISB Field Laboratory
	Analysis Suite 1: Ferrous Iron Sulfate	
	Chemical oxygen demand (COD)	
	Gamma Screens (Wells TSF-05A, -05B; TAN-25, -26, -31 only)	Radiation Measurements Laboratory (RML)
N	**Nutrients:** Phosphate Ammonia	ISB Field Laboratory
Sp	**Splits:** Volatile organic analytes (VOAs) Ethene/ethane/methane	Off-Site laboratories
Mt	Total Metals	Off-Site laboratories
^{90}Sr	Strontium-90	
GS	Gamma Spectroscopy	
GA	Gross Alpha	
MB_1	Microbiological research	IRC
MB_2	Microbiological research	Off-Site laboratories

3.2.3 On-Site Analyses

As stated above, analyses were performed using a combination of on-Site and off-Site laboratories. On-Site laboratories include the ISB Field Laboratory, INEEL Research Center (IRC), and Radiation Measurements Laboratory (RML). Analyses conducted in the ISB Field Laboratory included bromide, iodide, alkalinity, ferrous iron, sulfate, chemical oxygen demand (COD), phosphate, ammonia, and field standard additions. Tables 3-3 and 3-4 detail the planned on-Site analyses for the reporting period. Deviations from the planned tasks for on-Site analyses are included in Appendix A. In general, deviations from planned tasks were a result of exceeding holding times for samples, not completing all planned analyses, and losing samples due to breakage.

In addition to the analyses deviations, two changes in analytical techniques conducted in the ISB Field Laboratory were made during the reporting period to improve accuracy and increase the measurement range. Starting June 3, 2002, a pH meter was used to determine the end point during the alkalinity analysis. Formerly, the end point was determined based on a color change, which was subject to the discretion of the laboratory personnel. Starting April 1, 2002, a color wheel was used to measure ferrous iron concentrations when values were above the upper concentration limit of 3 mg/L for the colorimetric method. Formerly, ferrous iron concentrations above 3 mg/L were reported as "> 3 mg/L."

Starting April 1,2002, QA improvements were made to assess and ensure accuracy and precision of analyses conducted in the ISB Field Laboratory. One improvement was the inclusion of field standard additions (matrix spikes) for alkalinity, sulfate, phosphate, and ammonia. Table 3-5 provides information about the samples used to perform field standard additions for each analyte. Field standard additions for alkalinity were conducted with the same sample used during the alkalinity analysis, whereas the remaining analytes required preparation of a separate sample. A second improvement was the analysis of standard solutions for ferrous iron, sulfate, COD, phosphate, and ammonia each day these analyses were performed. Also, starting April 1, 2002, all reusable glassware was washed in a bleach solution after each use.

Table 3-5. Field standard additions

Date	Sample ID	Well	Analytes
April 1, 2002	TPD60601A1	TAN-28	Alkalinity
April 3, 2002	TPD61001A1	TAN-37A	Alkalinity
April 17, 2002	37A00101A1	TAN-37B	Alkalinity
April 29, 2002	PD500801A1	TAN-30A	Alkalinity
April 29, 2002	PD50080 13A	TAN-30A	Sulfate, Phosphate, Ammonia
June 3,2002	PD60 1301A1	TAN-1OA	Alkalinity
June 3,2002	PD60 1301F6	TAN-1OA	Sulfate
July 8, 2002	PD70 1301A1	TAN-1OA	Alkalinity
July 8, 2002	PD70 1301F6	TAN-1OA	Sulfate
August 5,2002	PD80 1401A1	TAN-D2	Alkalinity
August 5,2002	PD80 1401F6	TAN-D2	Sulfate
September 9, 2002	PD90 1301A1	TAN-1OA	Alkalinity
September 9, 2002	PD90 1301F6	TAN-1OA	Sulfate
October 8, 2002	PD 100301A1	TAN-26	Alkalinity
October 8. 2002	PD 100301F6	TAN-26	Sulfate

Additional on-Site analyses were performed at the IRC and the RML (Table **3-4).** Analyses conducted at the IRC included VOCs, ethene/ethane/methane, propionate/ butyrate/acetate/lactate, and microbiological research samples. Gamma screening was performed at the RML.

3.2.4 Off-Site Analyses

Samples were also sent to off-Site laboratories for analysis of tritium, VOC splits, ethene/ethane/methane splits, total metals, strontium 90, gamma spectroscopy, gross alpha, and microbiological research samples. Off-Site analysis laboratories, locations, and the dates that samples were sent to each laboratory are detailed in Table **3-6**. Only one deviation from the planned tasks occurred (Tables **3-3** and **3-4)** for the off-Site analyses. The holding time for microbiological samples shipped to the University of California at Berkeley on September 17, 2001, was exceeded as a result of a nationwide shut down of air traffic; the samples were shipped as soon as air shipments resumed.

Table **3-6**. Off-Site analvses locations

Off-Site Analvses	Laboratorv/Location of Analvses	Dates of Analvses
VOC Splits	Severn Trent Laboratories–St. Louis, Earth City, MO	Quarterly from August 2001 to August 2002
Ethene/ethane/methane Splits	Southwest Research Institute, San Antonio, TX	Quarterly from August 2001 to August 2002
Tritium	General Engineering Laboratories, Inc., Charleston, SC	Monthly from August 2001 to October 2002
Total Metals	Southwest Research Institute, San Antonio, TX	August 2001
Total Metals	Southwest Laboratories of Oklahoma, Inc., Broken Arrow, OK	Quarterly from November 2001 to August 2002
Strontium 90	General Engineering Laboratories, Inc., Charleston, SC	Quarterly from August 2001 to August 2002
Gamma Spectroscopy	General Engineering Laboratories, Inc., Charleston, SC	Quarterly from August 2001 to August 2002
Gross Alpha	General Engineering Laboratories, Inc., Charleston, SC	November 2001
Microbiological Research	University of California at Berkeley, Berkeley, CA	Monthly from August 2001 to February 2002

3.2.5 Geochemical Monitoring

During this reporting period, two different manufactured multiparameter water quality instruments, both capable of collecting water quality data (in situ and during well purging), were used. In situ data results are presented in Section 4.1.4 and the collected data are on the attached CD. Data collected during well purging are presented in Appendix D (see attached CD-ROM). Hydrolabs, manufactured by Hydrolab® A Hach Company Brand, were used to collect the field data parameters temperature, oxygen reduction potential (OW), pH, dissolved oxygen, and specific conductance during well purging and during in situ deployment in a subset of ISB wells. In situ specific conductance data were used to qualitatively assess distribution of electron donor. In situ temperature, pH, and O W data were used to qualitatively assess suitability of aquifer conditions for ARD. Hydrolabs were originally also used during well purging to determine the required purge times, as indicated by the stabilization of the purge parameters; however, sufficient stabilization data have been collected to determine an appropriate purge

time for each well. Hydrolabs were used during these standard purge times and the results were recorded, as required by the PDO SAP.

During this reporting period, Hydrolabs were frequently deployed in wells TAN-31, TAN-37, TAN-28, and TAN-30A. All Hydrolabs deployed in situ were removed for field standardization approximately once per month and usually redeployed the following day. In TAN-31, a Hydrolab was deployed throughout the reporting period. TAN-37 contained one Hydrolab at the A depth (i.e., a DataSonde unit, all other Hydrolabs were MiniSonde units) from the beginning of the reporting period through December 3, 2001. Starting December 11, 2001, two Hydrolabs were deployed in TAN-37 at the A and B depths and remained at those locations for the rest of the reporting period. Hydrolabs were deployed in TAN-28 and -30A starting September 25, 2001. The Hydrolab was removed from TAN-28 on August 22, 2002, and from TAN-30A on October 28, 2002. For the time periods reported, Hydrolabs may have been removed for periods greater than a few days, but not longer than 1 month. Also, a Hydrolab Diver was deployed in TAN-25 on June 27, 2002, that collects only specific conductance and temperature data. Deployment and removal dates for all Hydrolabs are detailed in Appendix C. Hydrolab operational issues for the reporting period—including use, locations of deployment, routine maintenance, and other issues—are also detailed in Appendix C. Routine maintenance included removal and redeployment for field standardization; changing dissolved oxygen membranes, Teflon junctions, and batteries; and routine downloading of data.

On August 8, 2002, a Multi-Parameter TROLL 9000, manufactured by In Situ, Inc., was first deployed in a TAN well (TAN-28). As of October 28, 2002, only well TAN-31 contained a deployed Hydrolab, as Trolls had been deployed in wells TAN-28, TAN-30A, TAN-37A, and TAN-37B (see Appendix C). Although Trolls have the capability to collect data during well purging, Hydrolabs were used to collect field data parameters during well purging for this reporting period.

3.2.6 Water Level Monitoring

Analysis of data in the 2001 ISB Annual Performance Report (INEEL 2002a) recommended maintaining transducers in wells TSF-05, TAN-25, and TAN-31 and reporting data for these wells in future ISB annual reports because data from these three wells showed discernable mounding resulting from sodium lactate injections in TSF-05. Based on these recommendations, groundwater elevations were measured using pressure transducers connected to data loggers in wells TSF-05, TAN-25, and TAN-31 for the sodium lactate injections during the reporting period, with the exception of the September 5, 2002, and October 30, 2001, injections. Water level monitoring data were used to determine whether or not sodium lactate injections have resulted in localized changes in permeability around TSF-05 and to observe localized water level rises (i.e., mounding) resulting from sodium lactate injections in TSF-05. The results of this monitoring are presented in Section 4.1.5 and discussed in Section 5.3.1 of this report.

3.3 Waste Management

As in previous years, Resource Conservation and Recovery Act (RCRA) -listed waste was generated as a result of ISB sampling activities and was managed in compliance with the requirements of the *Waste Management Plan for Test Area North Final Groundwater Remediation Operable Unit 1-07B* (INEEL 2002c). This waste included potentially contaminated wipes, sample bottles, personal protective equipment (i.e., gloves), sample residue from field analyses, sample rinsate, and purge water. Removal of all solid materials and sample residue from field analyses performed in the ISB Field Laboratory was coordinated with INEEL Waste Generator Services (WGS). Unaltered sample rinsate and purge water was transported to the New Pump and Treat Facility (NPTF) for processing following each sampling event in accordance with TPR-6641, "Purge Water Injection Procedure." Waste management issues that

directly affect **ISB** sampling, such as waste stream additions and corrective actions taken for misplaced waste streams, are detailed in Appendix A.

3.4 Groundwater Modeling

Groundwater modeling was used to support the **ISB** remedy component. The overall goal of the modeling activity was to develop a predictive tool that can be used to simulate electron donor transport and distribution under various electron donor injection strategies. The specific scope of the modeling activities included:

- The update, improvement, and calibration of an existing preliminary model (Sondrup et al. 1998) Available water level data, COD, specific conductance, and injection flow rates were used for model calibration.
- Modeling of the electron donor distribution using two injection scenarios:
  - Scenario 1–This scenario used the same mass but half the concentration injected using a single injection well, TSF-05
  - Scenario 2–This scenario included the simultaneous injection into two widely spaced injection wells.

3.4.1 Modeling Strategy

The following process was used to accomplish the tasks described above:

1. Confirm applicability of codes used in preliminary model
2. Establish boundary and initial conditions
3. Define property zones, injection rates, and injection duration
4. Calibrate flow model by adjusting hydraulic properties to match observed head changes induced from injections
5. Calibrate pathline model by adjusting effective porosity to observed specific conductivity peak arrival times
6. Calibrate COD transport model by adjusting transport properties to match observed COD data
7. Use the calibrated model to perform and evaluate the two injection scenarios described above.

3.4.2 Modeling Activities

This section summarizes the activities performed for each of the steps listed above. A complete description of these activities is presented in the *TAN OU 1-07B ISB Groundwater Model Development and Initial Performance Simulation* (INEEL 2002d).

3.4.2.1 Setup and Calibration of Flow Model. The preliminary model (Sondrup et al. 1998) used the MODFLOW and MODPATH groundwater codes, which are industry standards developed by the United States Geological Survey (USGS). The Groundwater Modeling System (GMS) pre- and post-processor and data analyzer were also used. Contaminant transport during this activity was simulated using the MT3DMS code, which uses the output from MODFLOW for the flow component.

The model used the same planar domain as the preliminary model; however, the vertical domain was extended downward to include the open intervals of all wells within the modeled zone. The previous model grid was refined around the injection wells, including the addition of a hypothetical injection well for Scenario 2 above. The flow model required the assignment of boundary conditions, initial conditions, hydraulic properties, location of injection and monitoring wells, and the fluid injection rates. Typically, one or two continuous injections were simulated for each injection scenario; the simulation periods were about 50 to 120 days.

The flow model was calibrated using observed head changes (mounding) in surrounding monitoring wells (TAN-25 and TAN-31) and the injection well during injection in TSF-05. Two sodium lactate injections, one from PDP-II and one from PDO, were used for calibration.

3.4.2.2 Particle Transport Model Calibration. The particle tracking model was calibrated to observed specific conductance peak arrival to obtain an effective porosity. Specific conductance data for sodium lactate injections were obtained from in situ Hydrolab™ monitoring. In this approach, the specific conductance from the sodium lactate injection is used as a conservative tracer to estimate arrival times and hence, advective velocity. Breakthrough curves obtained from in situ data from wells TAN-25 and TAN-31 were used for this effort. The effective porosity value was varied in the model to match travel times and peak arrival times.

3.4.2.3 Chemical Oxygen Demand Transport Model Calibration. The model was calibrated to match the COD distribution resulting from sodium lactate injection in TSF-05 on January 10, 2001. COD data from TSF-05A, TSF-05B, TAN-25, and TAN-31 were used. COD concentrations at TAN-37 were too low to be useful for the calibration. It was assumed that first order decay adequately represented COD degradation. Calibration was performed by fitting the model simulations to observed COD breakthrough curves. This was done by varying the transport parameters, effective porosity, and hydraulic conductivity.

3.4.2.4 Injection Scenario Simulations. As described above, two injection scenarios were simulated using the recently calibrated model. Scenario 1 involved the injection of the same mass as the PDP-II injections (1,320 gal 60% sodium lactate) but at half the concentration (~3% sodium lactate). Scenario 2 involved injection of dilute concentrations at a hypothetical well just west of TAN-37 simultaneously with injection in TSF-05.

The output of these model runs was in the form of COD breakthrough curves and normalized COD concentrations at TSF-05B, TAN-25, and TAN-31. Injection Scenario 2 also simulated the arrival and concentrations at two hypothetical monitoring wells located north and south of existing wells TAN-28 and TAN-30A.

3.5 2002 Tracer Test

The distribution of the electron donor was observed during the field evaluation phase to be a critical parameter for effectively implementing ISB at the OU 1-07B hot spot (DOE-ID 2000). As shown by the results from the field evaluation, essentially all locations that received an adequate supply of electron donor showed complete dechlorination of VOCs to ethene. As described in Section 3.4, the initial TAN ISB model was calibrated using available data to simulate the areal and temporal distribution of the electron donor. COD was selected as a single parameter that could be numerically modeled for various injection scenarios to predict the resulting extent of ARD in the aquifer (this is based on the assumption that ARD will occur in areas that receive sufficient electron donor). After two ISB injection scenarios were evaluated with the model, it was recommended that additional data be obtained to better characterize transport properties in the hot spot, including COD sorption and decay rates, COD breakthrough curves at

TAN-25 and TAN-31, and effective porosity and hydraulic conductivity of the source area (INEEL 2002d).

As a result of this recommendation, a tracer test was performed July 29–August 8,2002, using ISB wells TSF-05, TAN-25, TAN-26, TAN-31, TAN-D2, TAN-37A, TAN-37B, and TAN-37C. The 2002 Tracer Test Work Plan, located in Appendix A of the ISB PDO Work Plan (INEEL 2002b), provided the guidance for this activity. The objective of the 2002 Tracer Test was to address five data gaps resulting from the modeling activities. These data gaps included:

Data Gap 1—Determine the porosity in the vicinity of TSF-05 relative to results from the pre-bioremediation tracer test conducted in 1998 (Wymore, Bukowski, and Sorenson 2000)

Data Gap 2—Determine the porosity near the edge of the residual area

Data Gap 3—Determine the retardation factor for the electron donor

Data Gap 4—Determine the first-order degradation rate of the electron donor measured as COD

Data Gap 5—Determine the actual lactate and lactate by-product fermentation rates.

The basic strategy of the tracer test consisted of two stages in order to address the data gaps above. The necessity of performing the tracer test in two stages was based on the assumption that the sodium lactate injection solution is retarded during transport relative to ambient groundwater. This is primarily due to variations in fluid density and viscosity, which resulted in different hydraulic conductivities. The first stage of the test consisted of the injection of a conservative tracer (bromide) with potable water. This provided data to estimate porosity at the source area. These results were then compared with those obtained from the 1998 Tracer Test in order to address Data Gap 1 above. This comparison indicated any changes in the porosity of the area surrounding the injection well as a result of ISB activities. The second stage of the test consisted of the injection of a conservative tracer (iodide) during a normal sodium lactate injection. This was done to provide data to estimate porosity near the edge of the residual area (the second data gap above) by measuring iodide breakthrough curves at the outer wells (TAN-D2 and TAN-37). In addition, the second stage of the tracer test addressed the remaining three data gaps above by providing information to determine electron donor fate and transport parameters required for groundwater modeling. The retardation factor (Data Gap 3) was determined using the relative velocities of the iodide tracer and the sodium lactate. COD decay (Data Gap 4) was determined using the retardation factor, porosity, and COD concentrations measured over time in select wells. Finally, lactate and lactate by-product fermentation rates (Data Gap 5) were determined using the same methodology as Data Gap 4 but using lactate and individual volatile fatty acid (VFA) data rather than COD.

In order to implement this strategy, the tracer test was divided into the following five phases. Table 3-7 illustrates the sequence used to implement each of the phases.

Table 3-7. 2002 Tracer Test timeline.

	2002 Tracer Test Day											
	1	2	3	4	5	6”	7”	8	9	10	11	12+[b]
Phase 1												
Phase 2												
Phase 3												
Phase 4												
Phase 5												

a. No samples were collected or analyzed on Saturday or Sunday.
b. Indicates that the phase continued after the 1l-day fieldwork period.

1. Phase 1—Sodium bromide tracer and potable water were injected into TSF-05. 299 L (79 gal) of sodium bromide solution (36 kg of sodium bromide mixed with potable water) was injected as a slug for 26.3 minutes at 11.1 L/min (3 gal per minute [gpm]) along with potable water that was injected continuously for 6 hours and 38 minutes at 75.7 L/min (20 gpm) on Day 1 of the tracer test.

2. Phase 2—Sodium iodide tracer was injected with sodium lactate and potable water into TSF-05 during a routine 4X injection on July 30, 2002 (48 drums of 60% sodium lactate injected at 2 gpm [nominal flow rate], resulting in approximately 50,000 gal of 3% [nominal concentration] sodium lactate solution). 254 L (67 gal) of sodium iodide solution (72 kg of sodium iodide mixed with potable water) was injected as a slug for 22.3 minutes at 11.3 L/min (3 gpm) along with potable water and sodium lactate that was injected continuously for approximately 22 hours at 136 L/min (36 gpm) and 7.6 L/min (2 gpm), respectively, on Day 2 of the tracer test.

3. Phase 3—Groundwater samples were collected throughout the 11-day tracer test. Samples were collected at TAN-25 and TAN-31 every 4 or 6 minutes, respectively, beginning as soon as tracer was injected into TSF-05 on both Day 1 and Day 2 of the test. Sampling continued at this frequency until the concentration of tracer declined to less than 10% of the peak value for two consecutive samples. All wells were then sampled once or twice daily for the remainder of the tracer test.

4. Phase 4—Groundwater was analyzed at the OU 1-07B Field Lab for either bromide or iodide using Orion™ ion-specific electrodes (ISEs). COD was also analyzed at the OU 1-07B Field Lab. Lactate, propionate, acetate, and butyrate samples were analyzed at the IRC.

5. Phase 5—Data were analyzed using mathematical models representing groundwater flow and contaminant and tracer transport.

Analyses of samples taken from the injection line showed that the average bromide and iodide concentrations injected were 9,100 and 12,300 mg/L, respectively. All monitoring wells were purged prior to sample collection following low-flow sampling principles according to TPR-165, "Low Flow Groundwater Sampling Procedure." Variable speed submersible pumps were operated at approximately 3.8 L/min (1 gpm) to purge the wells. For wells TAN-25 and TAN-31, flow rates were decreased to approximately 1.9 L/min (0.5 gpm) after purging, and pumping was continuous while the wells were sampled every 4 and 6 minutes on Day 1 and 2 of the tracer test. Sampling locations and frequency details are described in Appendix A of the ISB PDO Work Plan (INEEL 2002b).

3.6 Alternate Electron Donor Laboratory Studies

While data from the field evaluation and PDP-I indicated that lactate is an effective electron donor for ARD in the TAN system, it was recognized that other alternative donors might be equally effective in terms of stimulating ARD, while at the same time being more cost-effective. Therefore, laboratory studies of AEDs were designed to assess the beneficial properties of AEDs relative to sodium lactate for achieving cost-effective dechlorination in the TSF-05 source area. The guidance for these studies is presented in Appendix E of the PDO Work Plan (INEEL 2002b). The properties determined to be important in this system were:

- ARD efficiency and cost-effectiveness

- Interfacial tension (IFT) between the AED solution and TCE

- Impact of the AED on the microbial community
- The metals content of the AED injection solution.

Studies were performed to address each of these four issues. The general strategy for each of the components is described below. Complete descriptions of the molecular studies, including the methods, results, and conclusions, are presented in Appendix E of this report.

3.6.1 Anaerobic Reductive Dechlorination Studies

In situ bioremediation operations conducted to date have demonstrated that the addition of sodium lactate as an electron donor stimulates complete ARD of TCE to ethene. The objective of this lab study was to evaluate whether other AEDs would be equally or more effective at stimulating complete ARD at TAN. Calculating the mass and/or molar balances of TCE and its ARD products and of the electron donor and its fermentation products when possible provided normalized comparisons for determination of relative efficiencies from which performance and cost were evaluated. The following tasks were performed during this component of the study:

1. Development of a TCE-dechlorinating laboratory culture from well TAN-25 groundwater
2. Inoculation of cultures amended with the AEDs feed-grade molasses, food-grade molasses, and cheese whey using the culture developed in Step 1
3. Comparison of the electron donor utilization and dechlorination efficiency between the AED and sodium lactate cultures
4. Evaluation of the cost-effectiveness of each of the AEDs for stimulating ARD compared to sodium lactate.

The initial laboratory cultures were developed in metal anaerobic bioreactors amended with sterile basalt, TCE, sodium lactate, and TAN-25 groundwater. They were periodically analyzed for TCE, its reductive daughter products, methane, ethane, ethene, lactate, acetate, propionate, and butyrate. The AED cultures were further developed in Erlenmeyer flasks modified for anaerobic sampling and amended with the bioreactor culture, fresh TAN-25 groundwater, TCE or PCE, and the respective electron donor. They were analyzed for the same parameters using the same methods described for the bioreactors.

The AEDs were evaluated based on analytical data to assess the electron donor utilization and ARD efficiency. The mass of each AED degraded was correlated to the mass of TCE dechlorinated to ethene to compare the cost-effectiveness of each AED relative to sodium lactate. The rationale was that if an AED was capable of relatively efficient ARD, but was significantly cheaper than sodium lactate, then it might provide significant cost savings for operations at TAN. The relative rate of ethene generation was also calculated for each AED and compared with sodium lactate. Again, the rationale was that if an AED could degrade TCE at a significantly faster rate, then the remedial timeframe for the residual source area at TAN might be shortened, thereby providing significant cost savings to the project. A complete description of the procedures used in these studies is presented in the final report *Fiscal Year* 2002 *Alternate Electron Donor Evaluation, Test Area North Final Remedy, Operable Unit 1-07B* (INEEL 2003a).

3.6.2 Interfacial Tension

During the field evaluation, the initial sodium lactate injections consisted of relatively high concentrations of sodium lactate (30 to 60%). It was observed that these high concentration injections resulted in significant increases in aqueous TCE concentrations (DOE-ID 2000). Because of distribution limitations resulting from the density of the high concentration solution, lower concentration (3 to 6%) injections were subsequently used. However, these lower concentration injections did not result in the dramatic TCE increases in response to lactate injections that were seen with the initial higher concentration injections. It was determined that the high concentration sodium lactate solution enhanced the dissolution of TCE from the residual source material to the aqueous phase (Sorenson 2000), a process known as Bioavailability Enhancement Technology™ (B.E.T.™). In situ bioremediation of TCE source areas is limited by the availability of TCE in the aqueous phase. In other words, microbes cannot access TCE in the dense nonaqueous phase liquid (DNAPL) phase for degradation directly; dissolution to the aqueous phase must take place in order for biodegradation to occur. Therefore, the degradation rate of TCE is limited by the dissolution rate of TCE from the DNAPL to the aqueous phase. Consequently, enhanced dissolution of residual TCE DNAPL is highly beneficial to the effectiveness of ISB for treatment of source areas. Subsequent studies have been performed to assess and understand this enhanced dissolution effect observed at TAN. The indicator chosen to evaluate enhanced dissolution between various electron donor solutions and TCE DNAPL was IFT. The following provides a summary of the activities performed to evaluate the impact of several AED solutions on the IFT with TCE.

Interfacial tension is a measurement of the work required to increase the interfacial (contact) area between two fluids. Fluids with high IFT, like oil and water, will not mix easily. A low IFT implies that the fluids have an affinity for each other and will more easily achieve a homogeneous mixture. TCE is a hydrophobic compound, meaning that it does not have an affinity for water. Thus, in a residual TCE source area, the IFT between the residual TCE DNAPL and the ambient groundwater is relatively high. If an electron donor solution has a lower IFT with TCE than does the ambient groundwater, then injection of that solution through the TCE DNAPL source would enhance the dissolution and the subsequent bioavailability of the contaminant. Higher concentrations of injected donor would be expected to have a more dramatic enhanced solubility effect. This enhanced bioavailability of the TCE source would result in more rapid degradation and ultimately, in a shortened remedial timeframe.

Laboratory measurements of IFT between pure phase TCE and various concentrations of AEDs were performed to predict the extent of enhanced bioavailability (solubility) that could be achieved in the field with that donor. The purpose was to test potential AED injection concentrations to maximize IFT, while still achieving good distribution. Significantly reduced (> approximately 10%) IFT between lactate solutions and TCE only occurred at lactate concentrations greater than 30% (wt% sodium lactate), which, when injected at TAN, have resulted in excessive distribution to the deep locations (TAN-26 and TAN-37C). AEDs that significantly lower the IFT at lower solution concentrations were considered desirable. The AEDs evaluated were:

- Ethyl lactate and lactate mixture
- Sodium dipropionate
- Molasses
- LactOil™
- Wheypowder
- Unground lactose

- Ground lactose
- Purified dairy carbohydrate
- Unpurified dairy carbohydrate

The IFT measurements were performed in a laboratory using a specialized instrument called the Interfacial Tensiometer, which was developed at the INEEL (Herd et al. 1992). A drop of the AED solution was injected upwards into a cell containing the DNAPL TCE using a syringe pump. The interface between the two liquids formed an image that was captured by a video camera, magnified, and displayed on a computer monitor. The IFT was then calculated using the dimensions of the drop and the density difference between the two liquids.

3.6.3 Molecular Analysis

The sodium lactate-impacted microbial community within the TCE residual source area at TAN has performed nearly continuous ARD of all aqueous phase TCE to ethene for nearly 4 years. Optimization efforts are currently being performed to evaluate more efficient and cost-effective AEDs (as described above). One of the biggest concerns in using AEDs is the potential impact on a microbial community that has been acclimated to a sodium lactate carbon source. The concern is that the microbial community, specifically the dechlorinating populations, might be negatively impacted by the change from one donor to another resulting in a significant decrease in ARD efficiency. Therefore, laboratory analysis of TAN-derived TCE-dechlorinating cultures was performed to characterize the microbial community supported by various AEDs to determine the differences in the community structure and to assess the presence of dechlorinating microbes within the different cultures. The AED cultures evaluated were:

- Feed-grade molasses
- Food-grade molasses
- Cheese whey
- Sodium lactate.

The two techniques used to characterize the AED microbial communities were polymerase chain reaction (PCR) and terminal restriction fragment length polymorphism (T-RFLP). Both techniques focus on the 16S rRNA gene, which has been extensively studied in published literature. Databases containing the 16S rRNA genes of all known species of *Bacteria* and *Archaea* can be used to determine the relative sequence identity of an unknown organism within a microbial community. Directed PCR was performed on the AED cultures to amplify *dehalococcoides ethenogenes* (DHE), the only bacteria isolated to date that is capable of complete ARD of PCE to ethene in pure culture (Maymo-Gatell et al. 1997). T-RFLP is a microbial community fingerprinting technique that amplifies the entire community by PCR, and then separates each species into a chromatogram displaying the species on the X axis and the relative abundance on the Y axis. Some species within the AED culture chromatograms were identified using existing sequences of identified TAN bacteria. A complete description of the objectives, methods, and results is presented in Appendix E of this report.

3.6.4 Metals Analyses

Some sodium lactate products have been determined to contain concentrations of EPA TAL metals that exceed EPA drinking water MCLs. During the ISB field evaluation, the regulatory agencies agreed

that concentrations of metals in electron donor injection solutions could exceed drinking water MCLs by a factor of 10 without adversely affecting human health and the environment. This was based on the recognition that natural attenuation processes reduced concentrations between the point of injection and potential receptor locations. It was also agreed that new sources of sodium lactate, as well as potential AEDs, must be analyzed according to EPA Contract Laboratory Program (CLP) methods for EPA TAL metals. The following presents a summary of all metals analyses that have been performed for evaluation of AEDs at TAN. Although some of these analyses were completed during previous reporting periods, they are included here for completeness. The results are presented in Appendix E of this report. Metals analyses were performed by Southwest Laboratory of Oklahoma, Inc. for the following AEDs:

- Westway feed-grade molasses
- AM Agricultural Products feed-grade molasses
- International food-grade molasses
- Groeb Farms food-grade molasses
- Western Community food-grade molasses
- Sodium dipropionate
- Powdered cheese whey.

3.7 In Situ Bioremediation Operational Support Activities

In addition to the activities previously mentioned in the above sections, other activities took place during this reporting period to support ISB operations. Issues regarding problems or changes with sampling equipment, well maintenance activities, and health and safety changes are detailed in Appendix A. TSF-05 pump placements and curtailment of daily inspections are discussed below, with additional information included in Appendix A.

3.7.1 TSF-05 Pump Placements and Sampling

The pump used to sample TSF-05 (A and B locations) was removed from the well between sampling events for radiation control purposes. Ideally, the pump should equilibrate at the sample depth location for 24 hours prior to sample collection (Kearl, Korte, and Cronk 1992); however, this was not always possible given the radiological management issues. In most cases, the pump was set at depth A the week before sampling took place and moved to depth B immediately following sample collection at depth A. Depth B was then sampled on the following day. The specific dates and times of pump placements and sampling for both A and B depths during the reporting period are detailed in Appendix A.

3.7.2 Curtailment of Daily Inspections

Daily inspections for both the Air Stripper Treatment Unit (ASTU) and the Groundwater Treatment Facility (GWTF) are not required when these systems do not contain hazardous waste. Therefore, in an effort to minimize daily operational requirements, actions were taken to remove the hazardous waste from these two systems. These actions are detailed in two letters attached in Appendix A.

4. RESULTS

Results for the work discussed in Section 3 are presented in this section. Groundwater data are presented in Appendix D (see attached CD-ROM). Section 4.1 discusses the results from ISB groundwater monitoring activities in the following areas: electron donor distribution and utilization (Section 4.1.1), redox conditions (Section 4.1.2), and ARD (Section 4.1.3). Sections 4.1.4 and 4.1.5 present the results of in situ geochemical and water level monitoring, respectively. Results from the offsite metals and radiological analyses are presented in Section 4.1.6, and QA results are summarize in Section 4.1.7. Section 4.2 contains the sodium lactate metals results. Section 4.3 provides a summary of groundwater modeling results. Section 4.4 contains the 2002 Tracer Test results, and AED laboratory study results are presented in Section 4.5.

4.1 In Situ Bioremediation Groundwater Monitoring

As described in Section 3.1, different injection strategies were used during the reporting period in an attempt to achieve the desired distribution of electron donor throughout the source area. These injections are summarized in Table 3-1. The specific injections are noted by the volume (1X, 2X, or 4X), the nominal concentration (3 or 6%), and the date(s) of injection. For each electron donor parameter, results are discussed for each of the injections.

For each injection, spatial trends are reported by dividing the wells within the treatment cell into four groups. Wells TSF-05A, TSF-05B, TAN-25, and TAN-31 are referred to as source area wells because they are located within the secondary source area where electron donor utilization and ARD take place. Wells TAN-26 and TAN–37C are referred to as deep wells, as they are located at the base of the aquifer. Wells TAN-37A, TAN-37B, and TAN-28, and TAN-30A are referred to as downgradient wells and reflect the conditions downgradient of the source area. Wells TAN-D2, TAN-29, TAN-27, and TAN-10A are located in the outer areas of the treatment cell and are referred to as outside wells.

4.1.1 Electron Donors

Hydrogen (H_2) that is produced from fermentation of injected electron donor is what ultimately drives ARD in the subsurface. In order to understand whether an electron donor is efficiently stimulating ARD, its degradation pathway must be understood. The microbial utilization pathway of lactate and its fermentation products is illustrated in Figure 4-1. From Figure 4-1, the first process that occurs following the dissociation of sodium lactate in solution is the fermentation of lactate ($CH_3CH_2OCOO^-$). Lactate can be fermented via one of two pathways: (1) to propionate ($CH_3CH_2COO^-$), acetate (CH_3COO^-), carbon dioxide, and water (Equation 4-1); or (2) to acetate, water, carbon dioxide, and free hydrogen (Equation 4-2):

$$3\,CH_3CH_2OCOO^- \rightarrow CH_3COO^- + 2\,CH_3CH_2COO^- + H_2O + CO_2 \qquad (4\text{-}1)$$

$$CH_3CH_2OCOO^- + 2H_2O \rightarrow CH_3COO^- + H_2O + CO_2 + H_2 \qquad (4\text{-}2)$$

Equation 4-1 produces propionate and acetate at a stoichiometric ratio of 2:1 and does not directly produce free hydrogen. However, following lactate fermentation via Equation 4-1, propionate can be fermented to acetate, carbon dioxide, water, and free hydrogen through the following reaction (Figure 4-1):

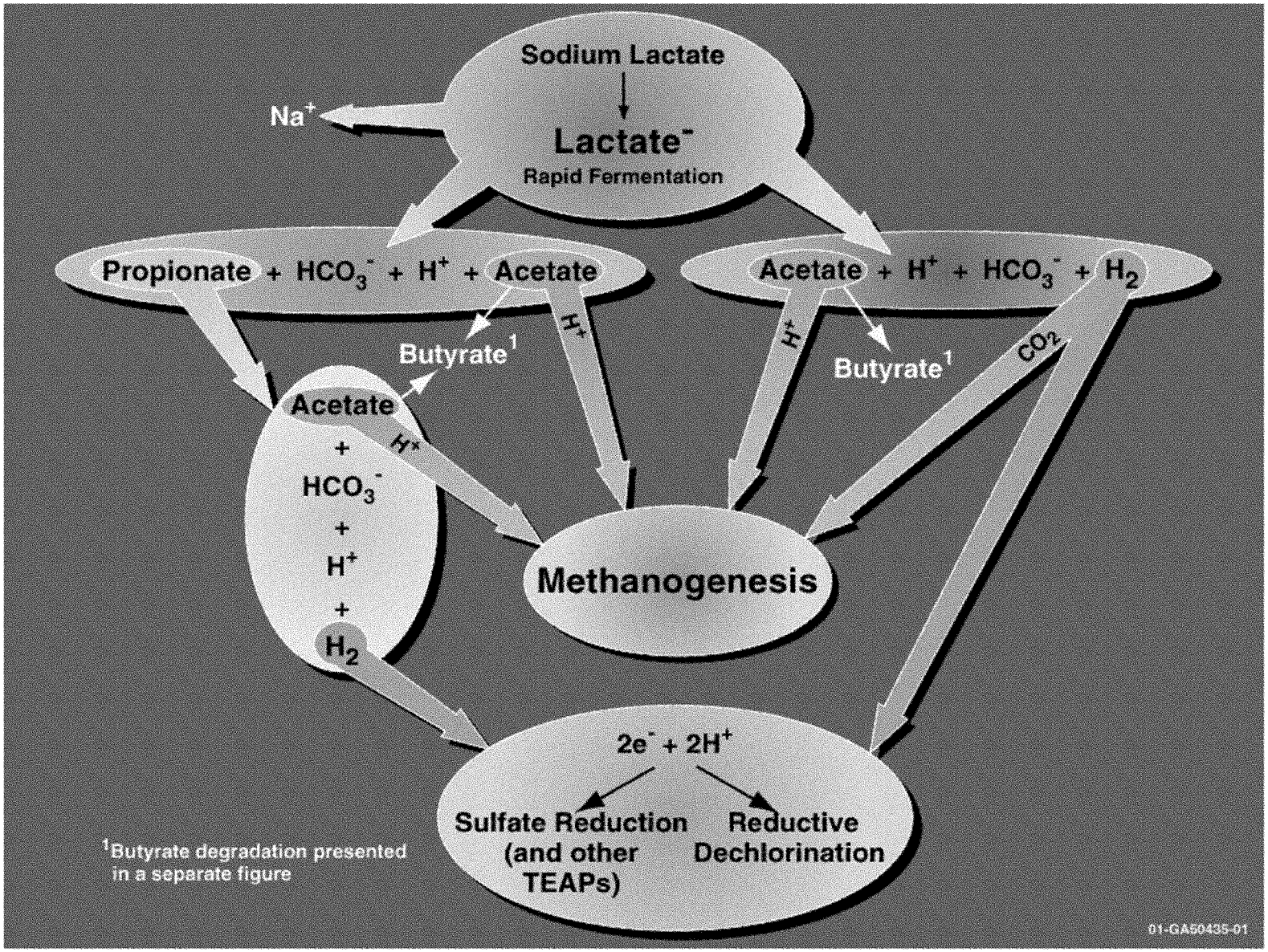


Figure 4-1. Microbial utilization pathways of lactate and its fermentation products.

$$CH_3CH_2COO^- + 3H_2O \rightarrow CH_3COO^- + H_2O + CO_2 + 3H_2 \quad (4\text{-}3)$$

Butyrate fermentation is not well understood. A hypothetical pathway for butyrate production is shown in the following reaction:

$$2\ CH_3COO^- + IT + 2H_2 \leftrightarrow CH_3CH_2CH_2COO^- + 2H_2O \quad (4\text{-}4)$$

Butyrate is generated when electron donor and H^+ concentrations are sufficiently high. As conditions change downgradient, butyrate can be fermented to acetate and hydrogen, which can stimulate both methanogenesis and ARD (INEEL 2000).

The fermentation pathway in Equation 4-2 does not appear to occur as rapidly as that of Equation 4-1, but is important in that it provides relatively low levels of free hydrogen that can be used for ARD. The fermentation of lactate in Equation 4-2 produces high levels of hydrogen, which also can be used for ARD. However, the hydrogen produced via the fermentation pathway in Equation 4-2 can be used to drive other processes such as methanogenesis (Figure 4-1). In contrast, the levels of hydrogen produced via the first fermentation pathway (Equation 4-1 followed by Equation 4-3) are below the threshold that methanogens can use. Therefore, the most efficient ARD will likely occur when the second fermentation pathway is dominant at a given site (Fennell, Gossett, and Zinder 1997). In order to increase ARD efficiency at TAN, the lactate injection strategy has been focused on maximizing the amount of time during which propionate and butyrate are the primary electron donors.

The importance of each fermentation pathway at TAN can be evaluated by examining the relative molar concentrations of propionate, acetate, and butyrate at locations within the treatment cell, while the overall distribution of electron donor can be tracked by monitoring COD. This section describes the distribution of electron donor (Section 4.1.1.1) and the utilization of electron donors (Section 4.1.1.2) within the treatment cell under various electron donor injection strategies.

4.1.1.1 Electron Donor Distribution. This section describes the different injection strategies and provides tables of pertinent data to show the impact of each injection strategy on the electron donor distribution at the various locations within the treatment cell. These tables include the well area (e.g., source); the well name; time elapsed after injection (the number of days following the start of injection before sampling was conducted); COD in mg/L; lactate, propionate, and acetate both as mg/L and as a molar percentage; and a molar ratio of propionate to acetate. It should be noted that the molar percentages might not sum to 100% because butyrate is not included in these tables. These data are also presented in Figures 4-2 through 4-12.

1X 6% Injection (September 5, 2001) **—** This injection consisted of approximately 12,000 gal of a 6% solution of sodium lactate and was completed within a 1-day period. This was the typical injection used during the PDP-II and PDO phases. In general, the impact on the source area wells was immediate, while the deep, downgradient, and outside wells saw little effect. The response observed for each well group is summarized below. Table 4-1 contains electron donor data following the September 5, 2001, injection.

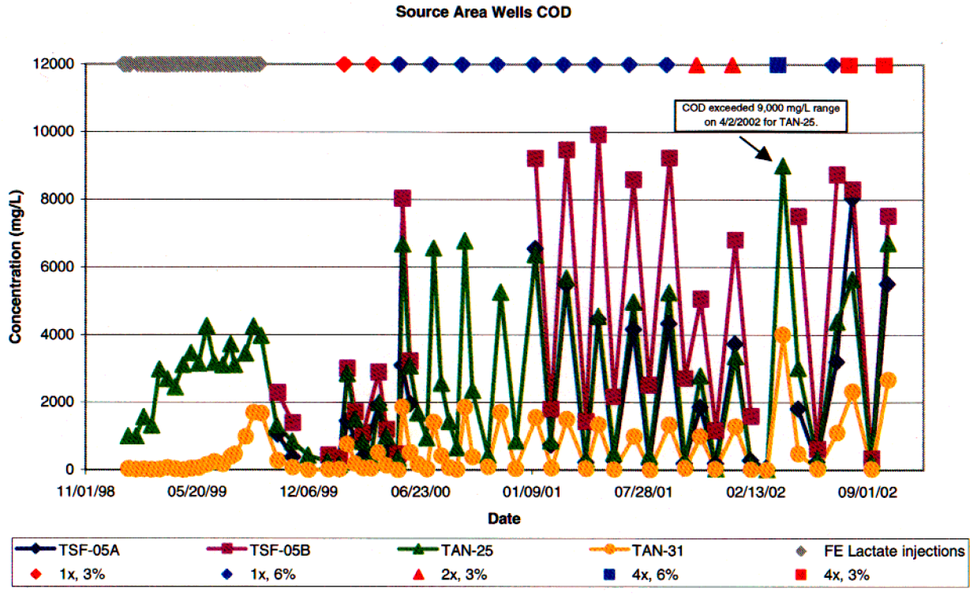


Figure 4-2. Source wells chemical oxygen demand.

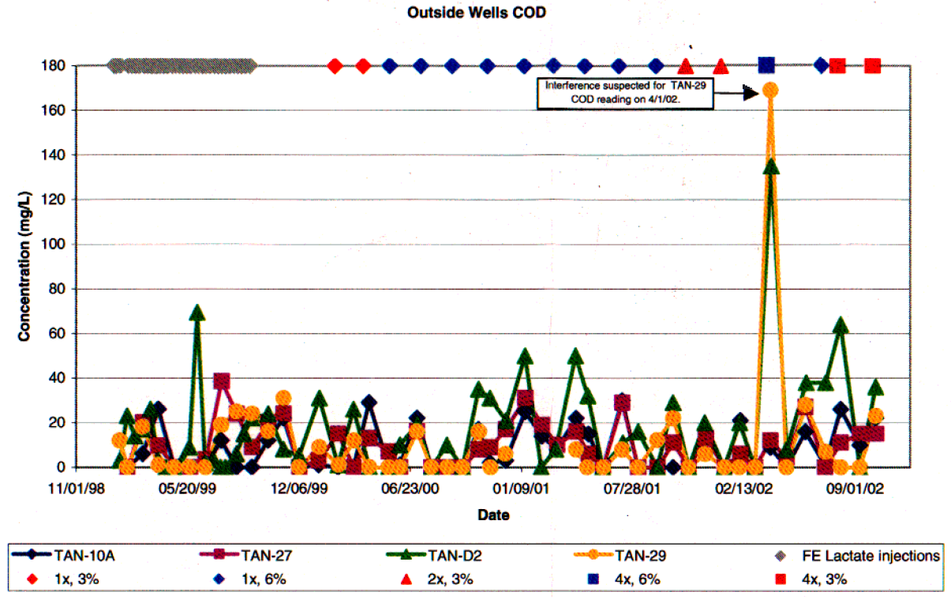


Figure 4-3. Outside wells chemical oxygen demand.

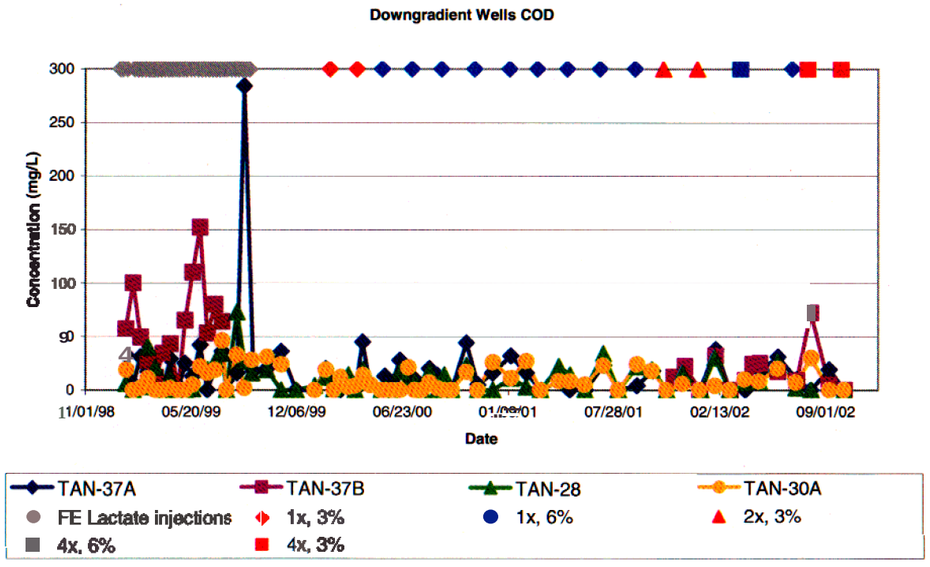


Figure 4-4. Downgradient wells chemical oxygen demand.

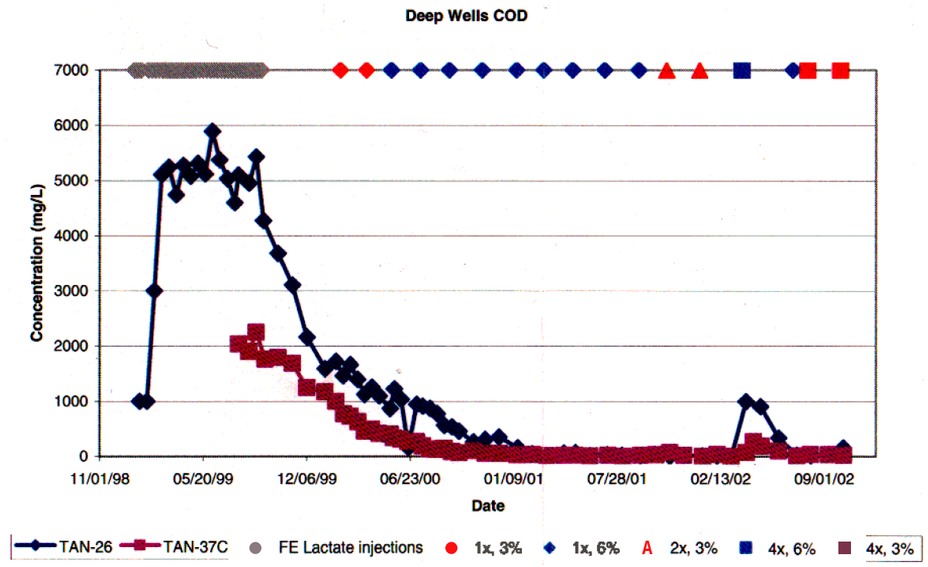


Figure 4-5. Deep wells chemical oxygen demand,

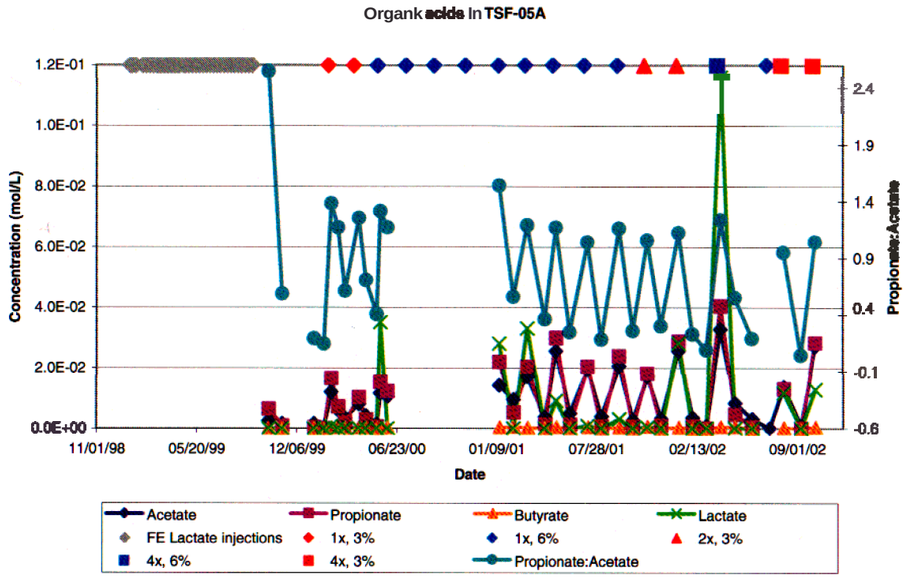


Figure 4-6. *Organic* acids in TSF-OSA.

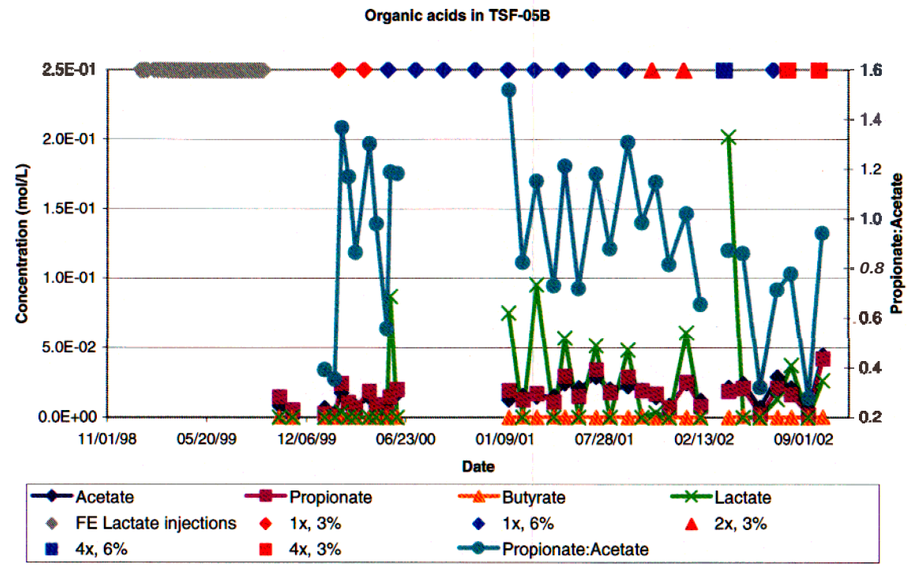


Figure 4-7. Organic acids in TSF-05B.

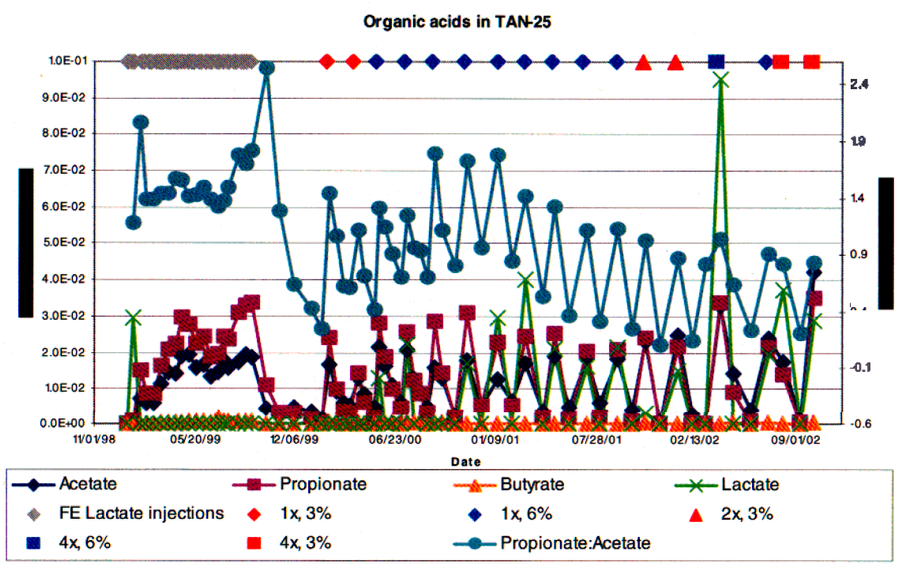


Figure 4-8. *Organic* acids in TAN-25.

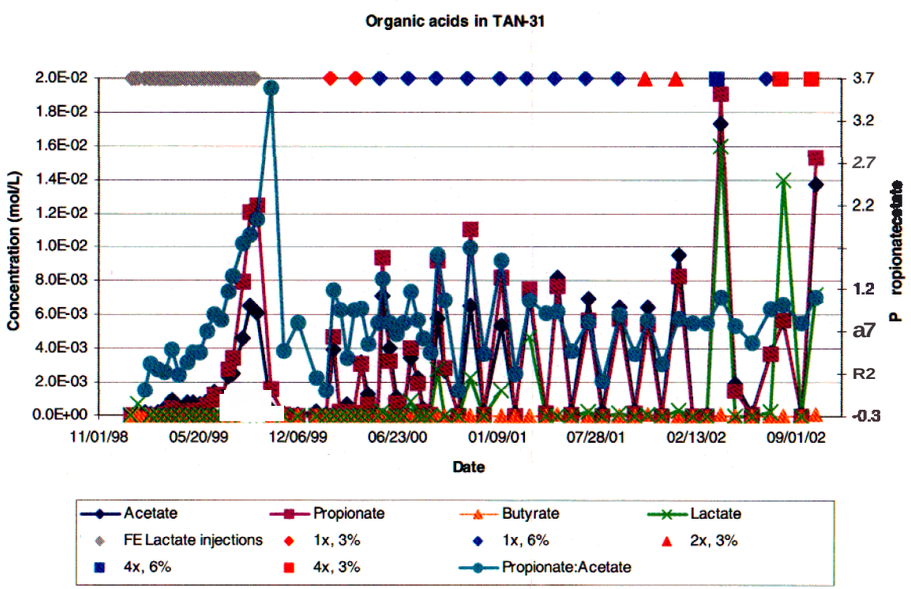


Figure 4-9. Organic acids in TAN-31.

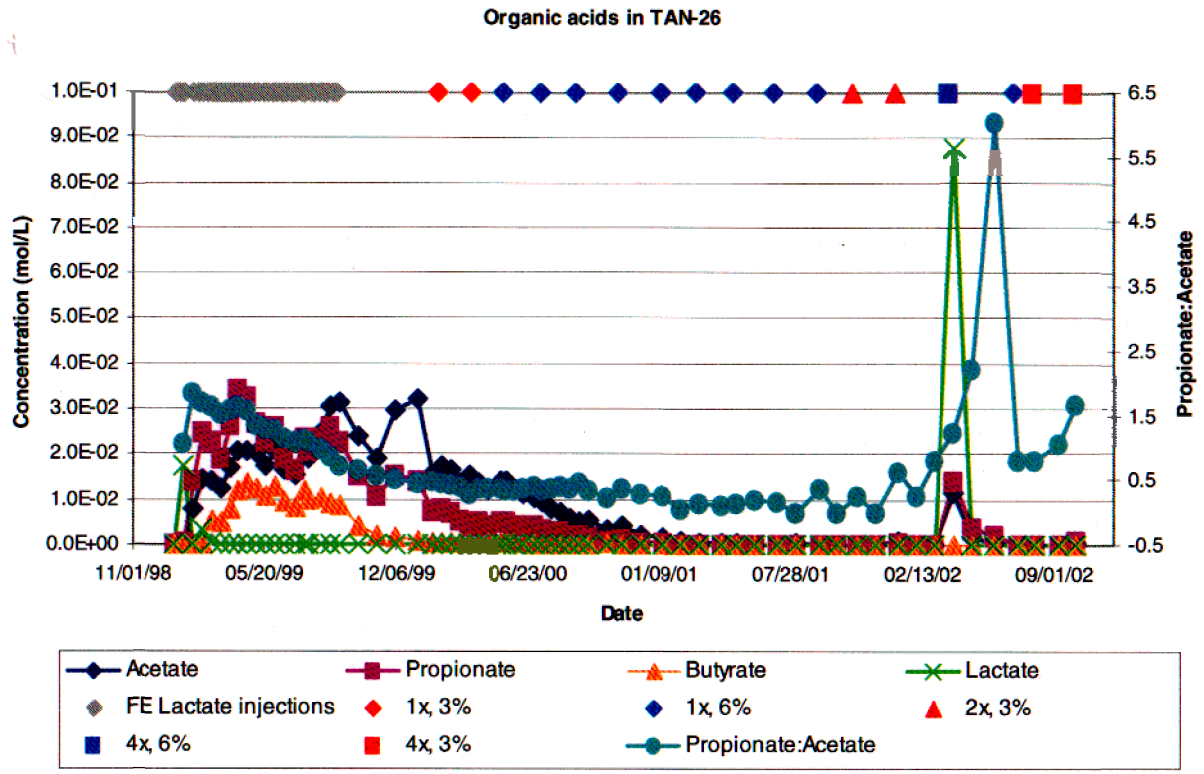


Figure 4-10. Organic acids in TAN-26.

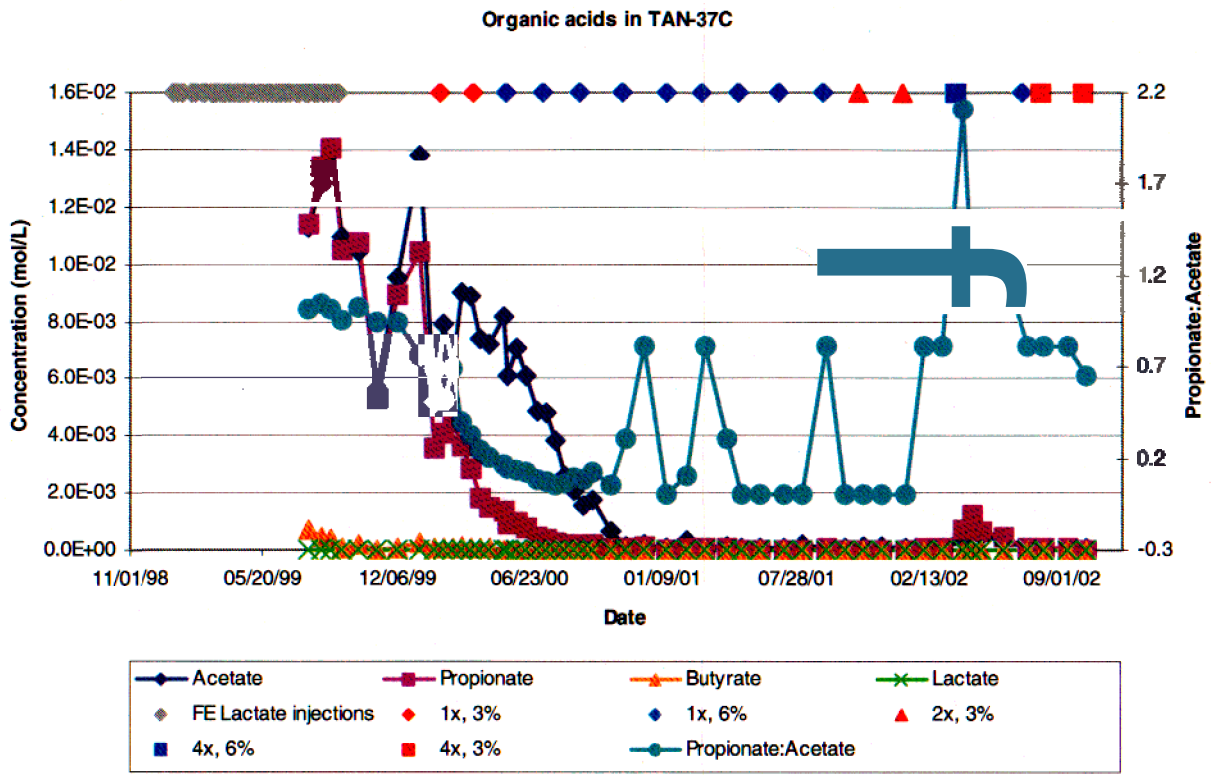


Figure 4-1[illegible] Or[illegible] acids in TAN-37C.

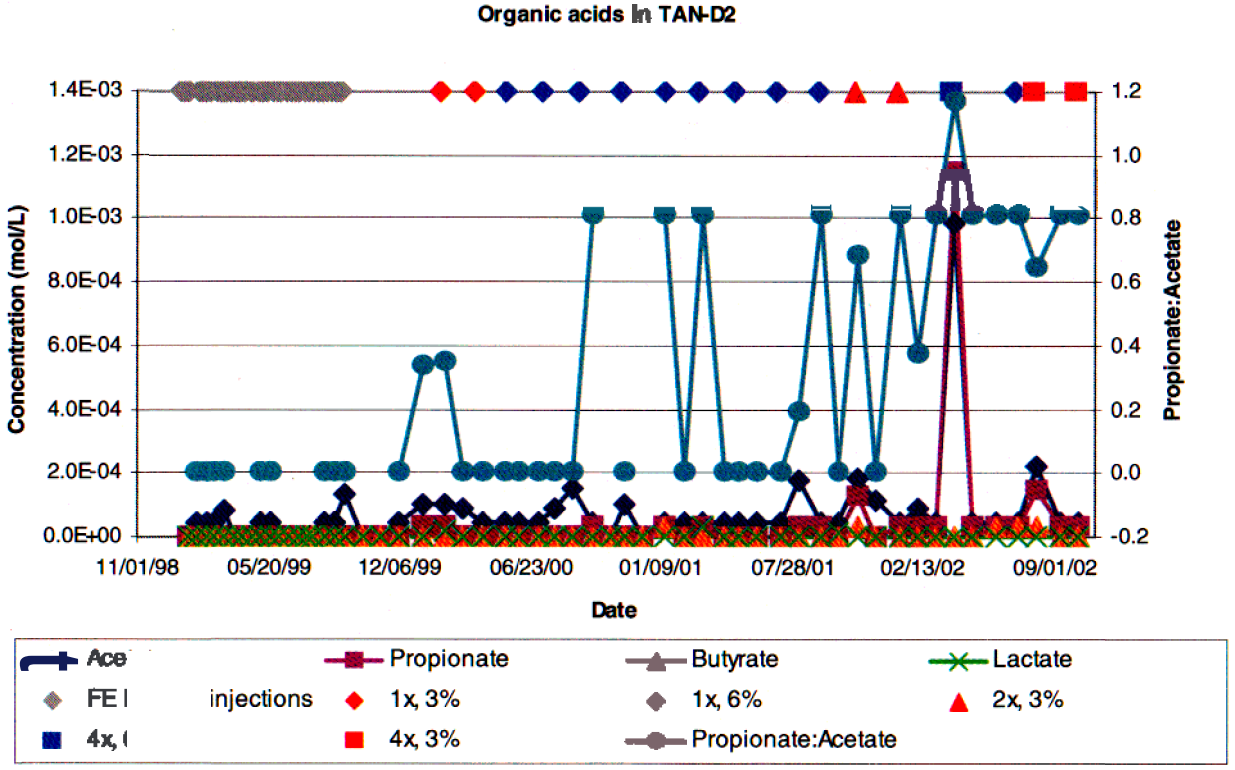


Figure 4-12. Organic acids in TAN-D2.

Table 4-1. Electron donor data for 1X 6% iniection on September 5. 2001

Well Area	Well	Time Elapsed After Injection	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Propionate:Acetate (molar)
Source	TSF-05A	6 days	4,329	277 7%	1,742 50%	1,213 43%	1.2:1
Source	TSF-05A	5 weeks	186	<0.223 N/A	51 20%	159 79%	0.3:1
Source	TSF-05B	7 days	9,234	4,309 48%	2,124 29%	1,314 22%	1.3:1
Source	TSF-05B	5 weeks	2,700	1.6 0%	1,400 49%	1,152 49%	1.0:1
Source	TAN-25	6 days	5,247	1,901 35%	1,504 34%	1,080 30%	1.1:1
Source	TAN-25	5 weeks	276	<0.223 N/A	71 19%	239 80%	0.2:1
Source	TAN-31	6 days	1,332	14.5 1%	425 47%	383 52%	0.9:1
Source	TAN-31	5 weeks	52	1.3 3%	12 29%	22 68%	0.4:1

2X **3% Injection (October 30,** 2001, **and January** 2, 2002) — This injection strategy, performed on October 30, 2001, and January 2, 2002, consisted of approximately 24,000 gal of a 3% nominal concentration of sodium lactate. Each injection was completed within a 1-day period. The larger volume was used with the objective of increasing the radial distribution of electron donor, particularly to the downgradient portions of the aquifer in the TAN-37A area. In general, electron donor was distributed to the source area wells but did not reach any of the deep, downgradient, or outside locations. The electron distribution in the source area wells is summarized below. Table 4-2 contains electron donor data following the October 30, 2001, injection. Table 4-3 contains electron donor data following the January 2, 2002, injection.'

At TSF-05A and TSF-05B, much more lactate was present following the January 2,2002, lactate injection as opposed the October 30, 2001, lactate injection, after which propionate was the dominant VFA. The overall differences in COD and VFA concentrations between these two lactate injection dates are likely a result of the longer delay (7 days versus 5 days for TSF-05A, and 8 days versus 6 days for TSF-05B) between injection and sampling, which allowed more time for utilization to occur.

4X **6% Injection (March** 25–28, 2002) — The objective of this injection strategy was to distribute electron donor to the downgradient area using a single injection well (TSF-05). The strategy used four times the solution volume (approximately 48,000 gal) and double the concentration (6% nominal concentration) of the previous two injections. The injection took place over 4 days. The rationale for this strategy was that the higher concentration (6%) and larger volume (4X) injected at half the frequency (every 4 months) would provide greater radial distribution of electron donor and might be sufficient to distribute donor throughout the system without having to drill a new injection well. Table 4-4 contains electron donor data following the March 25, 2002, injection.

Table 4-2. Electron donor data for 2X 3% iniection on October 30. 2001

Well Area	Well	Time Elapsed After Injection	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Propionate:Acetate (molar)
Source	TSF-05A	7 days	1,854	26 1%	1,319 50%	1,010 48%	1.1:1
Source	TSF-05A	5 weeks	189	<0.223 N/A	70 23%	189 76%	0.3:1
Source	TSF-05B	8 days	5,058	311 10%	1,232 48%	868 42%	1.2:1
Source	TSF-05B	5 weeks	1,167	trace N/A	501 44%	497 54%	0.8:1
Source	TAN-25	7 days	2,781	281 6%	1,733 47%	1,369 46%	1.0:1
Source	TAN-25	5 weeks	43	<0.223 N/A	<5 N/A	21 91%	N/A
Source	TAN-31	7 days	990	6.1 1%	395 45%	380 54%	0.81:1
Source	TAN-31	5 weeks	26	<0.223 N/A	<5 N/A	6.5 76%	N/A

Table 4-3. Electron donor data for 2X 3% injection on January 2, 2002.

Well Area	Well	Time Elapsed After Injection	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Propionate:Acetate (molar)
Source	TSF-05A	5 days	3,726	2,502 34%	2,094 35%	1,507 31%	1.1:1
Source	TSF-05A	5 weeks	284	<0.223 N/A	58 19%	203 81%	0.2:1
Source	TSF-05A	9 weeks	64	<0.223 N/A	5.5 8%	49 89%	0.1:1
Source	TSF-05B	6 days	6,804	5,402 55%	1,826 23%	1,446 22%	1.0:1
Source	TSF-05B	5 weeks	1,581	trace N/A	580 39%	716 59%	0.66:1
Source	TSF-05B	9 weeks	Sample not taken due to inoperable pump				
Source	TAN-25	6 days	3,357	1,325 24%	1,565 35%	1,465 40%	0.9:1
Source	TAN-25	5 weeks	156	<0.223 N/A	27 12%	156 87%	0.1:1

Table 4-3. (continued).

Well Area	Well	Time Elapsed After Injection	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Propionate:Acetate (molar)
Source	TAN-25	9 weeks	0	<0.223 N/A	<5 N/A	<5 N/A	N/A
Source	TAN-31	6 days	1,284	28.7 2%	604 45%	566 53%	0.86:1
Source	TAN-31	5 weeks	13	<0.223 N/A	<5 N/A	<5 N/A	N/A
Source	TAN-31	9 weeks	0	<0.223 N/A	<5 N/A	<5 N/A	N/A

Table 4-4. Electron donor data for 4X 6% iniection from March 25. 2002. to March 28. 2002

Well Area	Well	Time Elapsed After Injection	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Propionate:Acetate (molar)
Source	TSF-05A	7 days	>9,000	10,337 61%	2,952 21%	1,931 17%	1.24:1
Source	TSF-05A	5 weeks	1,809	1.4 0%	331 35%	487 63%	0.55:1
Source	TSF-05A	10 weeks	238	<0.223 N/A	43 16%	184 83%	0.2:1
Source	TSF-05B	8 days	>18,000	17,972 83%	1,375 8%	1,273 9%	0.87:1
Source	TSF-05B	5 weeks	7,506	1.8 0%	1,523 45%	1,430 53%	0.86:1
Source	TSF-05B	10 weeks	623	trace N/A	168 24%	424 74%	0.32:1
Source	TAN-25	8 days	>9,000	8,484 59%	2,451 21%	1,931 20%	1.03:1
Source	TAN-25	5 weeks	3,015	11.1 1%	639 37%	827 60%	0.62:1
Source	TAN-25	10 weeks	303	<0.223 N/A	70 18%	248 79%	0.2:1
Source	TAN-31	7 days	3,996	1,425 30%	1,396 36%	1,024 33%	1.10:1
Source	TAN-31	5 weeks	479	2.3 1%	109 43%	115 56%	0.77:1
Source	TAN-31	10 weeks	33	<0.223	7.9	11.3	0.6:1

Table 4-4. (continued).

Well Area	Well	Time Elapsed After Injection	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Propionate:Acetate (molar)
				N/A	33%	58%	
Deep	TAN-26	8 days	>1,000	7,802 78%	1,014 12%	674 10%	1.22:1
Deep	TAN-26	5 weeks	906	<0.223 N/A	262 68%	96 31%	2.2:1
Deep	TAN-26	10 weeks	336	<0.223 N/A	164 85%	22 14%	6.1:1
Deep	TAN-37C	9 days	72	<0.223 N/A	51 68%	19 32%	2.1:
Deep	TAN-37C	3 weeks	276	<0.223 N/A	90 53%	63 46%	1.2:
Deep	TAN-37C	5 weeks	190	<0.223 N/A	47 57%	29 43%	1.3:
Deep	TAN-37C	10 weeks	102	<0.223 N/A	33 54%	21 43%	1.3:1
Outside	TAN-D2	8 days	135	<0.223 N/A	84 54%	58 46%	1.2:1
Outside	TAN-D2	5 weeks	8	<0.223 N/A	<5 N/A	<5 N/A	N/A

Chemical oxygen demand data exceeded the dilution range of the method for TSF-05A, TSF-05B, and TAN-25 for the first data point after the injection. Lower fractions of propionate and acetate and higher lactate concentrations were seen immediately following lactate injection at TSF-05A, TSF-05B, and TAN-25, indicating a substantial lag period of lactate fermentation due to the higher concentration of donor. At TAN-31, the relatively equal percentages of the VFAs compared to the other source area wells may indicate increased utilization of lactate along the flow path to TAN-31.

This injection resulted in electron donor distribution to the deep wells. TAN-26 had the second highest COD concentration of any well 10 weeks following injection, which indicates that donor was relatively persistent at this location. Because donor does not frequently arrive at TAN-26, the lag-period of donor utilization was much longer than in the source area wells. This explains the relatively high fraction of lactate observed immediately following injection, as well as the persistence of propionate 10 weeks after the injection. No lactate data was obtained for TAN-37C following the April 17, 2002, injection, but it is likely that the majority of electron donor at TAN-37C was in the form of propionate and acetate due to the length of the flow path from the TSF-05 injection well to TAN-37C.

Electron donor was distributed to TAN-D2 for the first time following this lactate injection. Due to the distance from the injection well, the donor reached TAN-D2 in the form of propionate and acetate.

1X 6% Injection (July 1, 2002)**—**Electron donor data from sampling conducted in June 2002 indicated that concentrations of electron donor within the treatment cell were relatively low and would likely not

persist until the next injection, scheduled for July 30, 2002 (4X 3%). Therefore, on July 1, 2002, 12,000 gal of a 6% sodium lactate solution were injected to sustain the microbiological community until the next 4X injection, scheduled for July 30, 2002. The injection was completed within a 1-day period. Following the July 1, 2002, injection, COD increased in all of the source wells. Table 4-5 contains data for the 1X 6% injection on July 1, 2002.

Table 4-5. Electron donor data for 1X 6% injection on July 1, 2002.

Well Area	Well	Time Elapsed After Injection	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Propionate:Acetate (molar)
Source	TSF-05A	7 days	3,195	Sample lost due to breakage			
Source	TSF-05B	8 days	8,744	1,163 21%	1,515 33%	1,715 46%	0.71:1
Source	TAN-25	8 days	4,392	1,744 30%	1,582 33%	1,423 37%	0.90:1
Source	TAN-31	8 days	1,107	20 3%	271 48%	224 49%	0.98:1

4X 3% Injection—The July 30, 2002, and October 1,2002, injections consisted of approximately 48,000 gal of a 3% (nominal concentration) solution of sodium lactate. The first injection started on July 30, 2002, and ended on July 31, 2002 (2 days). The second injection started on October 1, 2002, and ended on October 3, 2002 (3 days). A 3% solution was used in order to enhance radial distribution without distributing donor to the deep wells (TAN-26 and TAN-37C), as was seen with the March 2002 4X 6% injection. The July 30, 2002, injection was performed in conjunction with a tracer test to support modeling of electron donor transport and utilization throughout the ISB treatment cell (described in Section 4.4). Table 4-6 contains electron donor data following the July 30, 2002 injection. Table 4-7 contains electron donor data following the October 1,2002, injection.

Table 4-6. Electron donor data for 4X 3% injection on July 30, 2002.

Well Area	Well	Time Elapsed After Injection	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Propionate:Acetate (molar)
Source	TSF-05A	6 days	8,046	1,038 30%	941 34%	801 35%	0.95:1
Source	TSF-05A	6 weeks	116	<0.223 N/A	<5 N/A	48 93%	N/A
Source	TSF-05B	6 days	11,088	3,336 50%	1,202 22%	1,250 28%	0.78:1
Source	TSF-05B	6 weeks	335	<0.223 N/A	130 21%	380 78%	0.28:1
Source	TAN-25	6 days	5,643	3,306 54%	1,020 20%	1,020 25%	0.81:1
Source	TAN-25	6 weeks	211	<0.223	22	84	0.21:1

Table 4-6. (continued).

Well Area	Well	Time Elapsed After Injection	COD (mg/L)	Lactate (mg/L) Molar%	Propionate (mg/L) Molar%	Acetate (mg/L) Molar%	Propionate:Acetate (molar)
				N/A	17%	81%	
Source	TAN-31	6 days	2,322	1,245 55%	416 22%	330 22%	1.0:1
Source	TAN-31	6 weeks	29	<0.223 N/A	<5 N/A	<5 N/A	N/A
Outside	TAN-D2	6 days	64	<0.223 N/A	10.5 44%	13.2 56%	0.64:1
Outside	TAN-D2	6 weeks	0	<0.223 N/A	<5 N/A	<5 N/A	N/A

Table 4-7. Electron donor data for 4X 3% injection on October 1,2002.

Well Area	Well	Time Elapsed After Injection	COD (mg/L)	Lactate (mg/L) Molar %	Propionate (mg/L) Molar %	Acetate (mg/L) Molar %	Propionate:Acetate (molar)
Source	TSF-05A	6 days	5,508	1,135 19%	2,056 41%	1,595 40%	1.0:1
Source	TSF-05B	7 days	7,515	2,356 23%	3,072 37%	2,638 39%	0.94:1
Source	TAN-25	7 days	6,714	2,572 27%	2,543 33%	2,495 40%	0.82:1
Source	TAN-31	7 days	2,664	639 20%	1,119 42%	813 38%	1.1:1
Deep	TAN-26	6 days	157	6.3 6%	49 58%	24 35%	1.7:1

4.7.7.2 Nectron Donor Utilization. As described above, concentrations of electron donor within the secondary source area were determined by measuring COD, lactate, and lactate fermentation products propionate, acetate, and butyrate. These data were used to estimate the electron donor distribution and the area of biological stimulation under the various injection strategies used during the reporting period. The effects of these different injections on electron donor utilization, specifically the first order degradation rates of lactate and its fermentation products, are presented for source area wells TSF-05A, TSF-05B, TAN-25, and TAN-31. Additional degradation rate estimates, which were based on data gathered during the tracer test, are presented in Sections 4.4.4 and 4.4.5.

The first order rate law for the consumption of reactant A is:

$$-\frac{d[A]}{dt}=k[A] \qquad (4\text{-}5)$$

where

[A] = concentration of **A**

t = time

k = fraction of A consumed per unit of time (rate constant).

Integration of Equation 4-5 with respect to time leads to:

$$[A] = [A]_0 e^{-kt} \quad (4\text{-}6)$$

where

$[A]_0$ = initial concentration of A

$[A]$ = concentration of A at time t.

The logarithmic form of equation 4-6 is:

$$\ln[A] = \ln[A]_0 - kt \quad (4\text{-}7)$$

This implies that the first order rate constant, k, can be determined by plotting ln[A] versus time. The plot is a straight line, with the slope equal to "$-k$" and the intercept equal to "$\ln[A]_0$". First order rate constants were calculated from lactate, VFA, and COD data from TSF-05A, TSF-05B, TAN-25, and TAN-31 using this method. Table 4-8 presents the estimated first order degradation rate constants for lactate after each of the different injections. The rate constants were calculated using the methods described above.

Table 4-8. First order lactate degradation rate constants during different injection strategies.

Well	Sept. 2001 1X 6%	Oct.30, 2001 2 x 3%	Jan.2, 2002 2 x 3%	Mar.25, 2002 4X 6%	Jul.30, 2002 4 x 3%	Oct.1, 2002 4 x 3%
TSF-05A	0.29	0.20	0.36	0.18	0.26	0.33
TSF-05B	0.28	0.47	0.55	0.32	0.30	0.35
TAN-25	0.33	0.28	0.33	0.18	0.29	0.18
TAN-31	0.08	0.15	0.20	0.15	0.26	0.31

The rate constants for TAN-25, TSF-05A, and TSF-05B were relatively low for the March 2002 4X 6% injection and highest for the January 2002 2X 3% injection. This is likely due to the negative impact of injecting a large volume of aerobic lactate solution into the anaerobic treatment area. The larger volume injections apparently required a longer recovery period to restore strongly reducing conditions and facilitate optimal fermentation.

The rate constants for TAN-31 were generally lower than those for the other source area wells. Also, unlike TSF-05A, TSF-05B, and TAN-25, the highest degradation rate constants for TAN-31 were for the July and October 2002 4X 3% injections, and the lowest constants were observed after the September 5, 2001, 1X 6% injection. Since TAN-31 is 50 ft crossgradient from the injection point, the lower volume injections (1X and 2X) did not achieve sufficiently high concentrations of lactate (6 to 29 mg/L) to support credible rate constant calculations. The high volume injections, however, achieved much higher concentrations of lactate at TAN-31 (640 to 1,400 mg/L) and resulted in more

reliable estimates of degradation rate constants. The lactate rate constants for wells TAN-25, TSF-05A, TSF-05B, and TAN-31 suggest that the high volume injections negatively impacted the degradation rate at TSF-05 and TAN-25 but resulted in greater distribution of electron donor to TAN-31, which positively impacted the biological activity at this well.

Table 4-9 presents the first order degradation rate constants for propionate for each of the different injection strategies. Overall, the rate constants for propionate were lower than for lactate. Unlike the lactate rates, the propionate degradation rate constant appeared to be a function of the concentration of the sodium lactate injections and not necessarily the injection volume. For example, the lowest degradation rate for all of the wells was observed after the March 2002 4X 6% injection, and the second lowest was after the September 2001 1X 6% injection. As described above, the lactate degradation rate declined after the March injection, suggesting that the presence of residual lactate likely inhibited propionate fermentation. The degradation rate constants observed after the 3% injections were similar for each individual well and were generally higher than the degradation rate constants observed after the 6% injections. TSF-05B had the lowest degradation rates compared to the other wells and also showed the highest lactate concentrations after every injection. TAN-31 had the highest propionate degradation rate constants after nearly every injection and the lowest lactate concentrations after every injection.

Table 4-9. First order propionate degradation rate constants during different injection strategies.

Well	Sept. 2001 1X 6%	Oct.30, 2001 2 x 3%	Jan.2, 2002 2 x 3%	Mar.25, 2002 4X 6%	Jul.30, 2002 4 x 3%	Oct.1, 2002 4 x 3%
TSF-05A	0.13	0.11	0.13	0.07	0.17	0.13
TSF-05B	0.01	0.03	0.04	NA	0.07	0.12
TAN-25	0.11	0.23	0.14	0.06	0.11	0.12
TAN-31	0.12	0.19	0.20	0.08	0.15	0.22

It should be noted that the propionate utilization rate estimates are net rates because production and utilization may be simultaneous. As such, the actual rates may be greater than the estimated rates. Despite this, the relations between the estimated rates discussed above should be valid (i.e., TAN-31 rates were greater than TAN-25 rates).

Table 4-10 presents the first order degradation rate constants for acetate during the different injection strategies. Overall, these rates were lower than either the propionate or lactate rate constants. Similar to propionate, however, the lowest acetate rate constants were observed after the March 2002 and September 2001 6% sodium lactate injections. Therefore, acetate degradation also appeared to be slower after high concentration injections. Lactate and propionate degradation both produce acetate; therefore, acetate accumulates with these compounds present. TAN-31 had the highest acetate degradation rates after all of the different injections, while TSF-05B had the lowest. Again, this is likely due to the combined effect of high concentrations of lactate within the injection well inhibiting acetate degradation, and aerobic injection solution negatively impacting fermentation.

Table 4-10. Acetate first order degradation rate constants during different injection strategies.

Well	Sept. 2001 1X 6%	Oct.30, 2001 2 x 3%	Jan.2, 2002 2 x 3%	Mar.25, 2002 4X 6%	Jul.30, 2002 4 x 3%	Oct.1, 2002 4 x 3%
TSF-05A	0.07	0.06	0.07	0.04	0.08	0.07
TSF-05B	0.01	0.02	0.03	0.004	0.04	0.08
TAN-25	0.05	0.15	0.08	0.03	0.07	0.07
TAN-31	0.09	0.15	0.19	0.07	0.14	0.21

As with the propionate rate estimates, the acetate degradation rate estimates are net rates because acetate production and utilization may be simultaneous. Thus, the actual rates may be higher. Also, it is worth noting that the relative magnitudes of the estimated degradation rates for lactate, propionate, and acetate were consistent with the thermodynamics for fermentation of these VFAs (i.e., lactate is most favorable, followed by propionate, and then acetate).

Tables 4-11 and 4-12 show the first order degradation rate constants using COD and total VFAs after the different injection strategies. In general, COD and total VFAs correlated well, which was consistent with historical TAN data indicating that the vast majority of COD within the treatment area are VFAs. These values estimate the degradation rate for the combined electron donor within the system for more general interpretations of electron donor utilization. Therefore, the estimated rates are less than lactate, but generally greater than either the propionate or acetate values. They also follow the same trend observed above, namely that the high concentration/volume injection in March 2002 resulted in much lower overall degradation rates than did any other injection. Overall, the TAN-31 degradation rates were the highest of the wells after all the injections, but especially after the large volume (4X) injections. This is likely due to the fact that more electron donor was reaching this well after the 4X injections, and also that the aerobic injection solution was not impacting this area as greatly as at TSF-05 and TAN-25.

Table 4-11. Chemical oxygen demand first order degradation rate constants during different injection strategies.

Well	Sept. 2001 1X 6%	Oct.30, 2001 2 x 3%	Jan.2, 2002 2 x 3%	Mar.25, 2002 4X 6%	Jul.30, 2002 4 x 3%	Oct.1, 2002 4 x 3%
TSF-05A	0.12	0.08	0.09	NA"	0.12	0.11
TSF05B	0.05	0.05	0.05	NA"	0.09	0.10
TAN-25	0.10	0.15	0.11	0.05	0.09	0.10
TAN-31	0.11	0.13	0.16	0.08	0.13	0.18

a. COD measurements were not taken after tlns injection.

Table 4-12. Total volatile fatty acid degradation rate constant during different injection strategies.

Well	Sept. 2001 1X 6%	Oct.30, 2001 2 x 3%	Jan.2, 2002 2 x 3%	Mar.25, 2002 4X 6%	Jul.30, 2002 4 x 3%	Oct.1, 2002 4 x 3%
TSF-05A	0.10	0.08	0.11	0.07	0.11	0.10
TSF-05B	0.04	0.03	0.07	0.06	0.07	0.11
TAN-25	0.09	0.18	0.11	0.06	0.11	0.10
TAN-31	0.11	0.17	0.19	0.08	0.16	0.21

Table 4-13 presents the molar propionate:acetate ratios observed for wells TAN-25, TAN-31, TSF-05A, and TSF-05B 6 to 8 days after the injections occurred. Overall, the values ranged from 0.78 to 1.31. The propionate:acetate in wells TAN-25 and TSF-05B appeared to decline after the 4X injections compared with the 1X and 2X injections. The TAN-31 propionate:acetate ratio, however, appeared to increase after the 4X injections began. This can be correlated to decreased lactate degradation rates after the 4X injections began for wells TAN-25, TSF-05A, TSF-05B, and to the increased degradation rate for TAN-31.